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CONTENTS.

VOL. VI.

Page

On the Phenomena exhibited by Dusty Air in the neighbourhood of strongly Illuminated Bodies. By Oliver J. Lodge and J. W. Clark. Part I. (Plate I.) 1

On some Experiments illustrating an Explanation of Hall's Phenomenon. By Shelford Bidwell, M.A., LL.B. (Plate II.) 29

On the Adjustment of Resistance-Coils. By Professor Silvanus P. Thompson, B.A., D.Sc., Univ. Coll. Bristol 47

Note on the Electric Conductivity and other Properties of the Copper-Antimony Alloys. By George Kamensky, Assoc. Royal School of Mines 53

Direct-Reading Electro-Measuring Instruments, and a Non-Sparking Key. By Professors W. E. Ayrton, F.R.S., and John Perry, M.E. (Plate III.) 59

On a Practical Point in connexion with the Comparison of Resistances. By W. N. Shaw, M.A., Emmanuel College, Cambridge. (Plate IV.) 71

Note on Hall's Phenomenon. By Herbert Tomlinson, B.A. .. 74

On the Determination of Chemical Affinity in terms of Electromotive Force.—Part VIII. By C. R. Alder Wright, D.Sc. (Lond.), F.R.S., Lecturer on Chemistry and Physics, and C. Thompson, Demonstrator of Chemistry, in St. Mary's Hospital Medical School. (Plate V.) 77

On an Integrating Anemometer. By Walter Baily, M.A. (Plates VI. & VII.) 115

On a Modified Resistance-Balance. By Professor Silvanus P. Thompson, B.A., D.Sc. (Plate VIII.) 121

On Eutexia. By Frederick Guthrie 124

Page

On a "Speed Indicator" for Ships' Propellers. By Sir Archibald Campbell of Blythswood and W. T. Goolden. (Plate IX.) 147

The Gas-Engine Indicator-Diagram. By Professors W. E. Ayrton, F.R.S., and John Perry, M.E. (Plate X.) 149

On Salt-Solutions and Attached Water. By Frederick Guthrie 169

On a new Apparatus for Colour-Combinations. By H. H. Hoffert, B.Sc., A.R.S.M., Assistant in the Physical Laboratory, South Kensington. (Plate XI.) 200

On a Method of Measuring the Electrical Capacity of a Condenser, and on the Determination by Electrical Observations of the Period of a Tuning-fork. By R. T. Glazebrook, M.A., F.R.S., Demonstrator of Experimental Physics at the Cavendish Laboratory, Cambridge 204

On the Thermal Relationship between Water and certain Salts. By B. Illingworth and A. Howard 212

Preliminary Notice of a new Sunshine-Recorder. By Herbert M'Leod, F.R.S. 216

A Magneto-electric Phenomenon. By C. V. Boys, A.R.S.M., Demonstrator of Physics at the Science Schools, South Kensington 218

Experiments on the Velocity of Sound in Air. By D. J. Blaikley. (Plate XII.) 228

On the Alterations in the Electrical Resistances of Metallic Wires, produced by Coiling and Uncoiling. By James Hopps, Superintendent of Workshops, Royal Indian Engineering College, Cooper's Hill (Plate XIII.) 235

On some Thermal and Volume Changes attending Mixture. By Frederick Guthrie 249

On the Determination of Chemical Affinity in terms of Electromotive Force.—Part IX. By C. R. Alder Wright, D.Sc. (Lond.), F.R.S., Lecturer on Chemistry and Physics, and C. Thompson, F.C.S., Demonstrator of Chemistry, in St. Mary's Hospital Medical School 275

A Capillary Multiplier. By A. M. Worthington, M.A. (Plate XIV. figs. 1 & 2) 351

Page
Note on a Point in the Theory of Pendent Drops. By A. M. Worthington, M.A. (Plate XIV. figs. 3–5) 355

The Influence of an Electric Current in Modifying the Rate of Thinning of a Liquid Film. By Prof. A. W. Reinold, F.R.S., and Prof. A. W. Rücker, F.R.S. 357

[At end of Volume.]

Proceedings at the Meetings, and Report of the President and Council for the Session 1884–85.

PLATES.

I. Illustrative of Messrs. O. J. Lodge and J. W. Clark's Paper on the Phenomena exhibited by Dusty Air in the neighbourhood of strongly Illuminated Bodies.

II. Illustrative of Mr. S. Bidwell's Paper on some Experiments illustrating an Explanation of Hall's Phenomenon.

III. Illustrative of Profs. W. E. Ayrton and John Perry's Paper on Direct-Reading Electro-Measuring Instruments, and a Non-Sparking Key.

IV. Illustrative of Mr. W. N. Shaw's Paper on a Practical Point in connexion with the Comparison of Resistances.

V. Illustrative of Messrs. C. R. Alder Wright and C. Thompson's Paper on the Determination of Chemical Affinity in terms of Electromotive Force, Part VIII.

VI. & VII. Illustrative of Mr. Walter Baily's Paper on an Integrating Anemometer.

VIII. Illustrative of Prof. S. P. Thompson's Paper on a Modified Resistance-Balance.

IX. Illustrative of Sir A. Campbell and Mr. W. T. Goolden's Paper on a "Speed-Indicator" for Ships' Propellers.

X. Illustrative of Profs. W. E. Ayrton and John Perry's Paper on the Gas-Engine Indicator-Diagram.

XI. Illustrative of Mr. H. H. Hoffert's Paper on a new Apparatus for Colour-Combinations.

XII. Illustrative of Mr. D. J. Blaikley's Paper on Experiments on the Velocity of Sound in Air.

XIII. Illustrative of Mr. J. Hopps's Paper on the Alterations in the Electrical Resistances of Metallic Wires, produced by Coiling and Uncoiling.

XIV. figs. 1 & 2. Illustrative of Mr. A. M. Worthington's Paper on a Capillary Multiplier.

„ figs. 3–5. Illustrative of Mr. A. M. Worthington's Paper on a Point in the Theory of Pendent Drops.

PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

APRIL 1884.

I. *On the Phenomena exhibited by Dusty Air in the neighbourhood of strongly Illuminated Bodies.* *By* OLIVER J. LODGE *and* J. W. CLARK [*].

PART I.

[Plate I.]

IN the course of a lecture on Dust and Disease given at the Royal Institution in 1870, Dr. Tyndall calls attention to, and fully illustrates by experiment, a dark or dust-free region which he had observed in the convection-currents rising from hot solids placed in the path of a powerful beam of light (see Proc. Roy. Inst. vol. vi. p. 1, also 'The Floating Matter of the Air'). He describes this dark stream as of surprising sharpness and definiteness, especially when it is seen above an ignited platinum wire, the line of sight being parallel to the wire but at right angles to the beam. Dr. Tyndall also gave two explanations of the phenomena—one of which he considered to be applicable when the solid is at a red or white heat; the other applicable when the body is at some more moderate temperature, such as that of boiling or even warm water. The first explanation is that the dust is absolutely burnt and consumed by the heat; the second is that the hot body warms the air in contact with it, which air therefore rises, dragging the dust after it but getting a slight start in advance of the dust, so that a thin stratum of the advance air from either side of the body is free from dust, and the mingling of the two strata constitutes the dark plane. This goes on continually as long as the convection-currents are produced by the body; and so the dark plane is permanent while the body is hot.

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[*] An abstract was read on February 9, 1884.

Prof. Frankland, in another paper on Dust and Disease, gives a still simpler account of the matter, and considers (Proc. Roy. Soc. vol. xxv. p. 542) that the observation proves that "a very large proportion of the suspended particles in the London atmosphere consists of water and other volatile liquid or solid matter." In other words, Prof. Frankland considers that the dust is simply dried up by the heat.

These three explanations seem to have been sufficiently plausible to satisfy those who may have examined or exhibited the phenomena discovered by Dr. Tyndall, until in 1881 Lord Rayleigh repeated and extended the original observation, "not feeling satisfied with the explanation of the dark plane given by the discoverer" (Roy. Soc. Dec. 21, 1882; 'Nature,' vol. xxviii. p. 139). He used a glass box to prevent draughts, and his hot body was usually a small copper spade which could be warmed from the outside of the box with a spirit-lamp. He called attention to the fact that the stream-lines round the obstacle follow the electrical law of flow, because the warm obstacle is itself the origin of the motion. He showed that smoke was not evaporated by being blown through a hot glass tube into sunshine, and he conclusively disproved any evaporation hypothesis by reversing the whole phenomenon: cooling the rod instead of heating it, and causing the dark plane to stream downwards.

Lord Rayleigh further suggested an hypothesis of his own to account for the dark plane in a simple mechanical manner, viz. that the curvature of the stream-lines near the surface of the obstacle was such as to cause the heavier dust-particles to be thrown outwards away from the body, and thus to leave a thin layer of air free from dust. To test this hypothesis he made a special centrifugal experiment with a whirling table, the direct result of which was negative; but it led to the observation of an apparent purification of air by contact with a solid, which if followed up might have led a good deal further. It was not followed up, however, though the remark is made that "it would seem as if this kind of contact was sufficient to purify the air without the aid of centrifugal force;" and the paper concludes with another test of the centrifugal force hypothesis, concerning which, finally, "no absolute conclusion can be drawn."

In the autumn of 1883 our attention was called to the matter by Lord Rayleigh's article in 'Nature;' and being struck with the apparent total collapse of all explanations hitherto offered, we proceeded to repeat the experiments with some care. The first result of any importance which we obtained was the fact that the dark plane hitherto observed to rise from a warm body, or to sink from a cold one, is only a continuation of a dark or dust-free *coat* of uniform thickness and sharp outline which completely invests the body; and we were led to the conclusion that this coat is the most important part of the phenomenon, because the up or down streaming-planes seem only to be that portion of the coat which is being continuously wiped off by convection-currents, the coat on the body being as continually renewed by some action not by us then understood. This fact, together with a few other results having reference mainly to the effect of electrifying the solid body, was communicated in a letter to 'Nature' (26th July, 1883, vol. xxviii. p. 297).

Since then we have continued the observations. We shall first describe generally the methods of experiment and the phenomena observed.

General Methods of Experiment.—In all cases the electric light has been employed to illuminate the bodies under examination in dusty media. For the examination in air and gases two principal forms of apparatus have been employed. Plate I. fig. 5 shows the glass box which has been used for ordinary air. The sides and one end are of glass, the other end is of wood and perforated with a hole for a cork; the top is also of wood, but provided with a wide slot, which can be closed by a glass plate, so as to allow the substance under examination to be illuminated from above, or by perforated wooden covers through which tubes, wires, &c. could be introduced when it was desired to test the electrical or other condition of the body under examination. The box is closed at the bottom by standing it upon a blotting-paper pad on one of Quincke's adjustable glass-plated supports. A fragment of magnesium wire burnt beneath the box served to introduce air laden with magnesic-oxide particles; and by removing the cover from the top of the box tobacco smoke could be readily blown in, or ammonic-chloride smoke by a current of air directed into the box through a heated tube containing ammonic chloride. The body under examination was supported near the glass end of the box either by means of the small adjustable clip shown in fig. 7, or passed through the cork in the opposite wooden end of the chamber. Fig. 6 illustrates this mode of support, the thin line representing a fine platinum wire attached to two stout copper wires through which a current to ignite the wire could be passed. Metal rods thus supported could be directly heated from without by means of a gas-flame, and, if desired, be insulated by passing through glass tubes in the cork.

Ordinarily the convergent beam of the electric light heated the body sufficiently, especially when it had been previously blackened in the smoke of burning camphor. For the examination in dry air and in different gases, either at the atmospheric or at lower pressures, the more complicated apparatus shown in fig. 8 has been employed. The larger end of the horizontal observing vessel is closed with a plane glass plate, through which observations were made. The other end of the vessel was closed with an india-rubber cork carrying two thermometers. The one served to indicate the temperature of the air within the vessel; the cylindrical bulb of the other was covered with camphor smoke and served as the surface upon which the coat formed, and also indicated its temperature approximately. Inert gases were dried by passing through concentrated sulphuric acid and through asbestos mixed with phosphoric anhydride; others, like ammonia, by passing through finely divided calcic oxide and caustic potash. The gases then passed through a wide tube containing ammonic chloride into the experimental chamber. By applying a gentle heat to this tube of ammonic chloride, the gas could readily be charged with its particles. For pressure in excess of the atmospheric, the form of apparatus shown in fig. 9 has been employed.

For the examination in liquids the box shown in fig. 10 was constructed. It has two plain glass sides. The double brass tube was about 0·5 centim. in diameter, and passed through a cork in the back of the box: this tube was heated either by a current of steam or by simply converging the beam from the lamp upon it. To render the liquid turbid, particles of dried ferric oxide have been found to answer well. With this form of apparatus, as also with those previously described, the light has been passed in through the side of the vessel, the body being examined through the glass in a line with its axis but at right angles to the direction of the beam of light.

The appearances presented by the body were observed either by the eye, through a hand lens, or through one of Quincke's microscopes provided with a micrometer eye-piece, indicated in fig. 8.

General description of Black or Dust-free Coat and Plane.—Before proceeding to a more detailed description of the appearances about to be described under varying conditions, we will briefly state what occurs when a rod of electric-light carbon, in ordinary air holding magnesic oxide in suspension, is illuminated at right angles to its axis at a place near the observed end by the converged beam of the electric light, and is viewed in a line with its axis. A water-cell conveniently intercepts a part of the radiation and renders the action slower. A careful examination at the first instant of turning on the light will usually reveal the dust-particles in close proximity to the surface of the rod, but in the case of a black solid they almost instantly leave it, and after a barely appreciable interval of time the upward and rapid convection-currents commence. There is now a thin ring of perfectly dust-free air and of great definiteness surrounding the carbon rod, a little thicker on the illuminated side, but distinctly traceable all round. On the top of the rod this ring is seen to stream upwards, the up-streaming portion being at first broad, but rapidly narrowing into a black line of very appreciable width, which is often traceable for a long distance through the turbid air of the box. The black ring surrounding the carbon cylinder is the dust-free *coat*, the black line rising from the top of it is the dust-free *plane*; the junction of the two the *base* of the plane.

On the under surface of the rod the particles are seen rushing up to the edge of the dark coat, not entering it, but curling away to the right and to the left, as if this coat were the real surface of the solid. Fig. 1*a* shows the rod in section surrounded by its coat and the plane on the top; fig. 1 shows also the paths followed by the dust-particles. It will be observed that the dust-particles follow the air-stream lines, moving *with* the air, not *through* it: any considerable motion of particles across stream-lines would soon obliterate the dark plane, whereas it is very persistent and is seen sometimes coiling itself up into a spiral. Another point of much interest is the distribution of the velocities of the dust-particles at different distances from the surface of the solid on a horizontal line perpendicular to its surface. In the case of carbon the velocities are all so great that individual particles are not readily traced, but under favourable circumstances it may be noticed that the particles reach their maximum velocity at an appreciable distance outside the black coat. It may be of interest here to state that on the surface of ice the coat and plane are absent, and the velocity distribution, considered as above, is apparently uniform up to a point so near the surface of the solid as to be indistinguishable from it with any degree of certainty.

We must now proceed to consider these appearances in greater detail, and the conditions under which they undergo modification. The contents of this paper may be conveniently summarized under the following heads:—

1. Experiments made with a view to ascertain the influence of size, shape, and nature of surface of the body examined.

2. Experiments made with a view to ascertain the effect of temperature, electric potential, and other conditions of the body.

3. Experiments made on bodies of different material.

4. Experiments made to observe the effect of pressure on the smoky medium.

5. Experiments made to examine the behaviour of different kinds of smoke—(α) volatile, (β) non-volatile.

6. Experiments on bodies which themselves give off smoke or vapour.

7. Experiments made to examine the conditions under which dust settles on surfaces.

8. Experiments made in media of different natures, *e. g.* different gases and liquids.

1. *Experiments on the Influence of Size, Shape, and Nature of Surface.*

(a) *Size.*—To see whether the size of the body had any marked effect on the width of the dark coat and plane, we have used cylinders of various thickness (*e. g.* iron wires ·15 and ·4 centim. diam., carbon rods ·7 and 1·22 centim.); but without temperature-measurements it is useless to exactly specify the results. We judge, however, that the thickness of the dark coat is independent of the size of the body (other things being the same), but that the rising dark plane is best marked on rods of moderately large diameter; certainly its base is bigger.

(b) *Shape.*—In our early experiments, when examining the appearances of the dark plane, we used copper scraps cut and bent into very various shapes; but we found the dark coat on all of them, and that the up-streaming of the dark plane was a simple matter of stream-lines; so we need only specify the results for a few of the more important shapes. In the great majority of cases we used a simple round rod, and its appearance has been already described. A flat horizontal plate or spade, a centimetre or less in width, shows a coat all over its under surface, very thin coats at its edges where the currents are violent, and a dark plane rising from a broad base, continuous with the dark coat on its upper surface. On a horizontal flat copper plate, 6 centim. wide, the coat on the upper surface is very thick, being little disturbed by currents. Its outline is not perfectly sharp, and it hovers or wavers about, some portions being thicker than the rest, and appearing likely to form upward streamers, though they seldom do. There is a certain amount of up-streaming from the coat, mainly from near the edges. On perforating the plate with a hole of about 0·07 centim. in diameter, a thin line of dust-laden air rises through the black coat on the under surface of the plate, and emerges into the black coat on the upper surface like a miniature volcano. If it emerge into dusty air the small smoke-column is sometimes seen thinly edged with black from having passed so near a solid.

A vertical flat plate has good coats and a plane. With thin mica or copper, ·003 inch thick, the coats are rather thicker near the top of the plate than near the bottom, and the dust touches the plate near the bottom, as proved by a deposit of dust which forms there. Blackening the surface increases the thickness of the coats.

A hemicylinder of sheet-copper was examined (*a*) with the concave side turned towards the light, (*b*) turned upwards, and (*c*) with the concave surface turned downwards. Its appearance in position *a* is shown in fig. 2; its interior is lined with a good dark coat. The coat was first seen on this piece. In position *b* a coat surrounds the surface, and from the two upper edges rise dark planes. We illuminate this from above by a 45° mirror. On the inner surface the definiteness of the boundary of the coat is not so good. Position *c* gives a dark plane from the top much as a round rod does; and inside also the dust-free coat is thick and well-marked. Wishing to make the air inside more stagnant, we glazed in its ends with mica, so as to stop even longitudinal currents, and now the gravitational settling of the dust broadened the inside dark coat; but the coat narrowed to its customary width when convection-currents were caused to circulate within the cavity. The different thickness of coat on curved surfaces is well shown by using the hemicylinder of glass, shown in fig. 4. The coat is evidently thickest where gravitation assists it, and thinnest where it opposes it.

The behaviour of very thin films is curious. Vertical glass films about ·0003 inch thick usually show no dark coat at all, and they either set up no convection-currents, or those which they set up are exceedingly sluggish. Strips of ordinary glass give good coats, the one on the illuminated side appearing first. It seems as if very thin films were incompetent to absorb enough radiation. (It has been incidentally noticed that these glass films, when freshly blown, adhere together when placed in contact. After standing in the air for a few hours this does not take place.)

A lump of rock-salt in ordinary air exhibited dark coats and a plane, but this might be due to moisture on the surface. A good plate of clear rock-salt, in air thoroughly dried with phosphoric anhydride, behaved just like the thin glass films, giving no coats and doubtful convection-currents. A plate of mica 0·002 inch thick absorbs sufficient radiation to exhibit the effects, though when the sheet was horizontal the coat on its upper surface was very badly marked. Mica showed an unexpected result, which is described later on.

Horizontal glass tubes filled with smoke, and immersed in the beam, have been examined by looking along the axis. The air inside is nearly stagnant, but the smoke collects in the axis of the tube, leaving a clear dark space or ring all round. The smoke settles also more slowly when the glass is thus warm than when it is at the temperature of the air.

(c) *Nature of Surface.*—Of three copper rods, one was tightly covered with blotting-paper, one with cotton wool, and the third left uncovered. They were all smoked with camphor-black, and exposed to the beam: the cotton-wool surface showed slightly the broadest plane. But the effect of such variation of surface is not marked, and is probably insignificant. Other experiments made with smooth electric-light carbon, and carbon roughened with sand-paper, led to the same conclusion.

2. *Experiments made on Solids at different Temperatures.*

To determine roughly the heating-power of the beam of light used, and to see at what temperature the dark plane became distinctly visible, a thermometer with its cylindrical bulb blackened with camphor-smoke was inserted horizontally into the box (fig. 5), and used as the solid to be examined. When the smoke was introduced, the thermometer read 21°. A few seconds after the light had been turned on, the dark plane was visible, and the thermometer read 21°·2. At 21°·5 the plane was good, but there was no coat visible to the eye. At 22° the coat appeared, and at 23° it was distinct. The thermometer was still rising rapidly, and soon attained 35°. The water-vessel, which had been used to moderate the violence of the converging electric beam, was then removed, and before long the thermometer was at 100° C., and was still rapidly rising. The coat and plane were now thick and exceedingly well-developed. In a second experiment, and examining through a hand lens, the coat was visible at 23°·7, and at 26° it was fairly thick. It must be remembered that the whole of the bulb was not warmed by the beam, and these temperature-readings are therefore only rough indications.

Probably common wood-charcoal gives the thickest coat of any substance we have examined; and although so bad a conductor of heat, the coat is not confined to the part of the solid immediately exposed to the beam. The thermometer was withdrawn from the experimental box, and the brass steam-tube out of the water apparatus (fig. 10) was inserted in its place; its surface was platinized. When this tube was heated by steam, the coat was rather thicker than when heated only by the beam from the lamp. The thickness of the coat on the steam-heated tube differs little from its thickness on the lamp-black thermometer-bulb at 100°.

The direct effect of temperature is ordinarily inseparable from the secondary effect of the convection-currents, which increase with the difference of temperature between the solid and the air. When the temperature of the solid is high, the coat is thick, although the convection-currents may be very rapid; for the cause which gives rise to the convection-currents also gives rise to the black coat: and it appears that the increased temperature facilitates the formation of the dark coat more than the increased velocity of the convection-currents thins the coat. Air-currents can be produced by blowing through a capillary tube on to the surface of the rod under observation, and the effect of such a current is to reduce the thickness of the coat; in fact the coat may thus be rendered so thin as to be imperceptible. The rod may be replaced by a metal tube, closed at one end and pierced laterally by a fine longitudinal slit or small hole in the examined region. An india-rubber tube attached to the other end of the tube allows air to be blown into the coat or plane. In this way the dark plane may be deflected in any direction, and by a very strong blast the coat rendered imperceptible. A body at the temperature of the air is probably destitute of a visible coat. On black surfaces it is hard to establish this point, as the light necessary for their examination warms them so rapidly. The careful study of a glass plate, or bright metal surface, however, reveals the fact that the coat is absent when first illuminated; its rapid formation may be seen. The coat appears to reach its maximum thickness very rapidly. At first we examined a body at the neutral temperature as it passed gradually from a temperature lower than that of the surrounding air to a higher. This method of examination led one of us to suppose, and to imply in the letter to 'Nature' (26 July, 1883, vol. xxviii. p. 297), that the coat was present on all bodies, whether warmer, colder, or at the same temperature as the surrounding air. But this method of examination is unreliable, as may be seen from the following.

A rod of carbon is cooled to −21° C. in a test-tube surrounded by ice and salt. The rod is quickly transferred to the glass box (fig. 5), smoke introduced, and the beam, filtered through water, turned on. The temperature being low, the first thing seen is a bright down-stream of particles. Very soon a dark streak in the middle of this appears, which dark streak widens and becomes a sharp and well-defined down-streaming dark plane, edged at first with the bright one, but later becoming free from it. The convection-currents are still rapid, and the only portion of a coat visible is the thickened base of the (inverted) plane. This incipient coat is soon traceable further.

This incipient coat becomes visible further round the rod, until the lower half is provided with a thin black coat. Soon the downward convection-currents cease, the plane loses its definiteness, and becomes confused with its thickening base and the coat itself, until the ill-defined mass of dust-free air turns around the rod of carbon, thus giving rise to a hazy ill-defined adventitious coat, which, if removed, would not be able to re-form at this temperature. The currents then begin to ascend, and this adventitious coat gives place to the true coat and sharp plane, already described as existing when carbon is warm. The appearance presented by the cold but warming rod seems capable of some modification, in consequence probably of variations in the rapidity with which the carbon is heated, and of its being an imperfect conductor. Thus occasionally the dark ill-defined dust-free space which exists at the bottom of the rod, just as the process of inversion commences, turns round towards the lamp, and may be succeeded by the ordinary black coat and a plane on that side, whilst, so far as has been ascertained, the coat may be partially wanting on the side remote from the lamp. Under these conditions one half of the base of the plane is more or less absent. This constitutes the unilateral plane shown in fig. 3.

3. *Experiments made with different Substances.*

Various substances have been examined in dusty air, such as copper, iron, zinc, carbon, glass, mica, selenite, vitreous selenium, Iceland spar, potash, rock-salt, bismuth, blotting-paper, black paper, white paper, chalk, polished silver, &c.; carbon moistened with various liquids; water, ice.

It may be stated, in a general way, that all these substances, when examined in the beam of the electric lamp, exhibit a remarkable similarity in their action towards the dust in the air, although they no doubt exhibit differences in the thicknesses of the coats. This is almost certainly exclusively dependent upon the temperature to which they are raised, and it is very probable that a thin layer of black camphor-smoke would make it difficult to distinguish between them. Ordinary wood-charcoal yields a coat remarkable for its thickness, in which respect it resembles electric-light carbon. Black solids and bad conductors favour the action by their high surface-temperature. Repeated heating to redness and cooling *in vacuo* certainly produces little, if any, diminution in the thickness of the coat of electric-light carbon.

Porous solids moistened with more or less volatile liquids yield wide coats, and sometimes downward black planes. In the dust-laden atmosphere they have been observed to give rise to a partial double coat and two planes. When moistened with two liquids of different boiling-points, no two distinct planes and coats were obtainable, although the boundaries of the observed coat and plane may not have been as distinct as in the case of a solid in merely smoke-laden air.

Liquid surfaces are capable of giving rise to dark planes of great distinctness in the dusty air above them. This may be well shown by attaching a thin horizontal platinum wire to the ends of two copper wires passing through the tube of a funnel, rendered water-tight by means of sealing-wax. Water is then introduced into the funnel until it is about to overflow. Above the surface of the water is the smoke-laden atmosphere of the box. The platinum wire just beneath the liquid surface is then warmed by means of a feeble current, and the light turned on: a clear and distinct plane can then be distinguished rising from the thin line of warmed liquid. If the whole liquid surface be allowed to get warm a thick dark coat is visible above it, and a large columnar dark plane rises from the centre.

Our experience with mica was interesting. The first small sheet which we tried was placed horizontally in the box with magnesic-oxide smoke. The light revealed little growing bushes or trees of aggregating magnesic-oxide particles. The mica was evidently electrical. Rubbed sealing-wax acted in a similar way, but so did an unrubbed rhomb of Iceland spar to a slight extent. We at first thought that the mica might be photo-electric like certain crystals observed by Hankel. All pieces of mica do not behave in this way. Pressure between the finger and thumb, writing upon the surface with a blunt point of cork, or with a pencil on a piece of paper laid upon the mica, all seem capable of producing the deposition of the white dust upon these portions, but in a lesser degree. There would seem to be a possible relation between these effects and the "Hauchbilder" of Moser (Wüllner, *Physik*, Bd. i. S. 416, Dritte Auflage). Perhaps the removal of moisture-condensing nuclei may not be without influence upon the correctness of his explanation. The action in the case of mica would not, however, seem to be wholly, nor necessarily, electrical, as the following observation would tend to show. A Chladni brass plate was casually used by the assistant as a desk upon which to support a piece of paper upon which he was writing with a pencil. Upon subsequently bowing the plate, after dusting Lycopodium upon it, the writing became legible upon the surface of the brass. This action of mica is not, so far as we have observed, produced by simple heating. With a slab of tourmaline cut perpendicular to the axis from a crystal belonging to Prof. N. Story Maskelyne, the effects of heating, cooling, and re-heating this pyroelectric crystal by the beam of light were very distinctly shown. We believe that some such simple and delicate method as that here indicated may be of use in the investigation and demonstration of such actions.

4. *Experiments made to ascertain the Effect of Pressure in the Smoky Medium.*

The apparatus for this purpose has already been referred to; it is shown in fig. 9. It could be connected with a water air-pump, which reduced the pressure to a few centimetres of mercury, or with a large iron cylinder, in which the air was condensed by pressure of the water-main. The open mercury manometer indicated a pressure of 4½ atmospheres (in excess of the atmospheric pressure).

Tobacco smoke was introduced by slight exhaustion, and the small rod of electric-light carbon, shown in section in fig. 9, was heated by the electric-light beam being converged upon it. Under an absolute pressure of 5½ atmospheres the convection-currents became very slow, the black plane wavy and unsteady, whilst the coat was so thin that only with the aid of the hand-lens could it be traced with certainty on the side of the carbon directly exposed to the heat of the lamp. The plane, moreover, was incomplete at its base—unilateral, a further indication that the coat was probably wanting on the colder or shadow side of the carbon-rod. Under a pressure of about 6 centim. the coat was wider than in air at the barometric pressure. The dependence of the thickness of the dust-free coat upon pressure was well marked; and already some preliminary numerical determinations have been made, which we hope will shortly enable us to determine the law of the dependence of the coat upon pressure with some degree of accuracy. The following figures for air serve to show that the thickness of the coat varies at different pressures. They were made with the apparatus shown in fig. 8.

Pressure of air, in centim. of Hg.	Thickness of coat, in centim.
75·9	·013
20·8	·027
10·9	·054
3·9	·083

The variation with pressure of course suggests ideas connected with the free path of molecules at the surface of the body; but the thickness of the coat is far greater than that ordinarily reckoned as the length of free path corresponding to the pressure.

The effects of electrification on the dust-free coats and the examination of electrical actions in dusty air generally were preliminarily noted in 'Nature,' July 1883, but the investigation of them is yet incomplete.

5. *Experiments with different kinds of Smoke.*

We have endeavoured to ascertain whether any of the phenomena obviously depend on a drying or on a combustion of the smoke-particles. Bearing in mind the very wide coat which surrounds an incandescent platinum wire, it seemed to us, even in this case, improbable that dust-particles were often burnt up by it, although we are well aware of the ease with which finely divided matter will oxidize. Chiefly with this object in view, we repeated an experiment adduced by Tyndall to show that combustion was a *vera causa* of the dust-free up-streaming air, but we used the incombustible and non-volatile particles of MgO. For this purpose we have employed a platinum wire, fig. 6, enclosed in the box fig. 5, and ignited by a current from a battery. The appearances are unchanged, and the air of the box rapidly clears; the white smoke being deposited upon the cold sides of the box. When volatile particles, such as ammonic chloride, are used, a thicker coat is observed at high temperatures than with magnesic oxide. This is probably in consequence of volatilization; for at low temperatures, such as 100°, no such difference is noticeable. When a rod of camphor is examined in air laden with magnesic-oxide particles, a dust-free coat and plane may be distinguished. But as the camphor gets gradually heated it volatilizes and makes the coat on the side near the lamp far wider than elsewhere. Hence it would appear that the volatilization of the camphor keeps back the dust-particles beyond the normal distance. The camphor-particles can be distinguished amidst the particles of MgO on the boundary of the coat and plane near the light, on account of their crystalline sparkling nature.

What influence the size of the dust-particles exerts upon the thickness of the coat has not yet been fully made out experimentally.

6. *Experiments on Bodies which themselves give off Smoke.*

We early noticed that a distinction had to be drawn between smoke given off from the warm body itself and smoke which belonged to the air external to the body. The latter seemed to be repelled from the body; the former seemed to come into contact with its surface.

If tobacco-smoke is blown on to an illuminated strip of common window-glass, the smoke nearest to its surface hovers tenaciously about long after the more distant smoke has disappeared; but a visible dark coat is still found to separate the dust from the surface.

There are many ways of getting a body covered by a layer of smoke. One way is to blow it on to its surface through a capillary tube ; another way is to pass the copper rod through the axis of a narrow glass tube fixed in a cork at the end of the box, so that the rod projects into the experimental glass box (fig. 5), and blow smoke through the tube. The smoke rushes along the surface of the rod, forming a sort of tube, but is gently carried away as the rod gets warmer, in the manner described, showing itself all the time as a white coat and plane inside the dark coat and plane which separate and keep back the general dust in the air of the box.

Another way is to let smoke ooze through holes in the sides of a tube upon which the light is allowed to fall. But the easiest plan is to use a substance which generates its own smoke, such as phosphorus. A common stick of phosphorus in ordinary air produces copious white fumes, which, being heavy, descend, and when illuminated a white coat and well-marked descending white plane are seen. The white coat is very thick, and hence probably it is that no portion of the black coat or plane is to be seen. If the air in the box is gradually dried, however, oxidation of the phosphorus so far diminishes as to enable an observation to be made upon the phosphorus in the particle-laden air before it again begins to emit smoke. This reveals the phosphorus surrounded by the dark coat and plane. But as the temperature rises the oxidation proceeds more rapidly, and the black coat and plane gradually become more obscure, as the smoke coming from the surface of the solid enters them.

7. *Experiments on the Settling of Dust.*

Black paper-sheets and metal plates blackened with camphor smoke have been arranged in various positions in a box full of the white smoke of magnesia. It is observed that those which are warm receive barely any deposit of dust, notwithstanding the large volume of air which has passed near them. This is not due to the deposit being blown away.

Of surfaces at the temperature of the air those seem to collect most dust over which the air is the most stagnant; the dust has time to settle on flat level surfaces by common gravitation unless the motion of the air over them is too rapid. Cold surfaces collect a large quantity of smoke, and become coated over with a thick white deposit, as if it were attracted by the solid. Among cold surfaces rank all those walls of the box which are not directly warmed by the beam of light. If warm smoke is blown through a tube on to such a surface it adheres very largely, giving a thick local deposit opposite the tube.

Impressions showing the dark plane can be obtained by placing glass plates near warm solids in dust-laden air; and we have copied such impressions of the dark coat and plane on to sensitive paper by ordinary photographic printing [*].

8. *Experiments in different Media.*

(a) *Gases.*—By far the larger number of our experiments have been conducted in common air, but we considered it highly important to observe the behaviour of various dry gases of very different density from air, and also to see whether any phenomena of the same kind could be detected in liquids.

With the apparatus shown in fig. 8, and already described, we have ascertained that hydrogen gives a much thicker coat, and carbonic anhydride a thinner coat, than is obtained in air, under conditions which we believe to be fairly comparable.

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[*] Mr. John Aitken would also appear, from an abstract in 'Nature' (31st Jan.), to have obtained these records upon glass. It is singular how closely many of his experiments run with ours.

The figures in the following Table will serve to indicate roughly the differences which have been observed :—

	Temp. of solid.	Temp. of gas in observing vessel.	Thickness of coat in centim.
Hydrogen............	41°	17°	·033
Ammonia	65	26	·013 (?)
Air....................	82	14	·020
Carbonic Acid	63	20	·011

The first column gives the temperature indicated by the thermometer upon the blackened bulb of which the coats were measured. The third column gives the measurements made at the middle of the bulb on the side near the light. In the middle column the temperature of the gas in the experimental chamber, as indicated by the second thermometer, is given.

The quantitative portions of this paper are as yet incomplete, and we consider the above figures only as indicating the differences provisionally. Some gases, moreover, appear to vary considerably in their action towards the camphor-smoked surface; and, in short, there are obscure conditions which affect quantitative results in a way which we do not yet fully understand.

(b) *Liquids.*—The outline of the method employed for the study of the appearances observed in liquids holding fine particles in suspension has already been described (fig. 10). The box is best filled with cold water from which the air has been expelled by recent boiling, and to which a little ferric oxide has been added, to render it turbid. When the beam of the lamp is now converged on to the surface of the empty brass steam-tube, there is usually to be seen a slightly dust-free space of liquid beneath the tube. Under the influence of the beam this becomes thinner, and two dust-free planes rise from each side of the tube, ultimately meeting upon the top of the rod, and often at first enclosing particles between them, as occasionally observed in gases. A dust-free black coat and plane are then seen, distinct but rather thin. This seems to be a permanent state so long as these conditions are preserved unaltered. The convection-currents are fairly well developed, and the velocity-distribution resembles that described for a warm solid in dusty air. If now a current of steam be sent through the brass tube, the convection-currents become more rapid, and the coat so thin that we are not certain of its existence. Moreover, the distinctly dust-free black plane is no longer quite certainly there, although a casual observation would probably lead to the conclusion that it was. A long fine up-streaming layer of liquid, differing from the surrounding liquid, *is* distinctly visible, and a very similar result is obtained from a platinum wire strongly heated by the passage of an electric current. There is no doubt that liquids holding small particles in suspension are capable of giving rise to appearances similar to those described in gases, and it seems that in a liquid an increase of temperature occasions a less rapid increase in the thickness of the coat than is the case with a gas; or, in other words, the coat is thinner at high temperatures such as 100° C. than it is at a lower because the convection-currents have more power to destroy it.

Examination of the Hypothetical Explanations already suggested.

At the commencement of the paper are given all the provisional explanations which have been hitherto suggested as accounting for the dark plane so far as we are aware. The existence of the coat renders several of them improbable, but they appear capable of direct disproof, thus :—

Any centrifugal-force hypothesis is negatived by the points of inflexion on the stream-lines of fig. 1, and more conclusively by fig. 2, where the white space between the parallel curved lines represents in section a hemicylinder of sheet-copper with its black coats. The convection of the stream-lines is here such as to whirl the particles into the coat rather than out of it. The evaporation and combustion hypotheses are disproved by the use of a non-volatile and incombustible smoke like magnesic oxide; also by the phenomena being observable in liquids.

There remains only the "distribution" hypothesis of

Tyndall (originally given Proc. Roy. Inst. 1870, vol. vi. p. 3), viz. that the dust lags a little behind the air as it starts off in a convection-current. It is not so easy to negative this, and in fact in some form or other it is certainly true that the dust does get filtered out of the air, being all made to keep outside the dark coat, while some of the air passes in. The only question is, Why does the dust get driven out of the air in this way? what is there near the surface of a warm body which keeps back the dust? A mere lagging behind of the dust particles by reason of their extra inertia seems to us a quite insufficient statement. The first formation of a coat on the surface of a solid before the convection-currents have started, and the case of the interior of a glass tube, may be adduced as negativing any purely convective explanation: the dust-free coat is seen not only on the outside of a tube where convection-currents are in full swing, but it is well marked also as an internal lining of the tube where the air and dust are both stagnant. The internal lining, though thick, is of irregular thickness, and has not the sharp boundary of the outside coat. The universal effect of convection-currents is to sharpen the boundary of the coat, but to thin it down. This is, indeed, a very important fact, and leads straight to the conclusion that the formation of the dark coat is an operation which requires time, though only a very short time, and that it is possible to carry off a great part of the coat more quickly than it can be renewed.

Suggested Explanations.

The provisional explanations which have occurred to us as possible during the course of the investigation have been very numerous, and have been mostly one after another discarded, and only one or two are at all worthy of being here mentioned.

One notion which occurred pretty early in the experiment, if it had held its ground, would have reduced the whole thing to the merest mechanical phenomenon, just as Dr. Tyndall's original ingenious explanation (to which, by the way, we were more than once tempted to revert) or Lord Rayleigh's centrifugal-force notion would, if true, have deprived the dark spaces of most of their physical interest. It was in the belief that something deeper than common mechanical principle was at the root of the appearances that we were originally tempted to examine them so closely; and we are not sorry that the barbarous simplicity of the notion now to be mentioned has failed to explain them, though at the same time we still believe it modifies the effects, and that sometimes notably. We call it the settling hypothesis, and it may be stated thus:—

Dust falls through fluids at a pace depending on the size of the particle and the viscosity of the fluid, but the relative settling velocity is not affected by the motion of the fluid, whether horizontal or vertical. We may regard all dust as constantly settling relatively to the fluid in which it is.

By so settling, it may leave dust-free spaces.

Under a horizontal plate, therefore, the dust might settle, and leave a clear dust-free coat; so it might also perhaps immediately under the middle of a round rod; and it is just conceivable that air from this clear space might get partially carried up and round the rod by convection-currents no faster than fresh settling kept on renewing it below.

It is undeniable that gravitation must assist the formation of coats on the under surface of plates, and must do its best to spoil any coat on the top. The action of gravitation in this way is described in various parts of the paper. It is impossible, however, for any one witnessing a really good dark coat under a warm rod, and seeing the rushing-up of the dust against the dust-free coat, to go away with the notion that gravitative settling has produced that sharp, definite, and thick coat against which the up-rushing dust-particles almost seem to rebound. The idea is irresistibly suggested of something keeping them forcibly off.

Moreover, suppose a plate to be originally at the temperature of the air: it has no coat. Turn on a powerful light: a coat instantly forms, and rapidly thickens under the eye before any convection has time to begin. It looks just as if the dust were driven out from its surface by some action which depends upon the temperature.

Again and again have we been driven to the notion of a molecular bombardment carried on from the surface of the body, by which the dust-particles are driven away like the vanes in Mr. Crookes's radiometer, or like drops in the spheroidal condition. But we were unable to take up precisely this position because of the enormous thickness of the dust-free coat as compared with the mean free path of an air-molecule at the ordinary pressure.

We then tried to develop a notion of an *extreme* free path: we thought whether the dust-particles might not be so easily moved that the impact of even a few molecules on their surface would be sufficient to drive them back; and we tried to imagine that, though the great bulk of the flying molecules only shoot a distance from the surface reckoned in hundred thousandths of a millimetre, yet a few, say an odd million or so per second, might escape collision for a distance of even half a millimetre, and that these might drive back the dust. The difficulty here would be to see why the boundary of dust and no-dust is as sharp as it is, though we tried to imagine that this was caused by the convection-currents, a definite amount of bombardment being necessary to drive back the dust when carried towards the surface at a given rate, and this definite bombardment being found at a definite distance from the surface. We were now fairly landed, by the observations we had made, on some molecular bombardment hypothesis or other, while before this we had been searching among all kinds of mechanical, electrical, and other notions of a vaguer kind. The necessity for some kind of bombardment explanation being thrust upon us, it was not long before we perceived that no considerations of free path were necessary, but that a differential bombardment on the two sides of a dust-particle would be sufficient to drive it back. In other words, a dust-particle would move from a region of greater pressure to a region of less, being urged by a force depending on the size of the particle and the pressure-slope.

Consider a warm flat vertical surface of copper. Adhering to the surface is a layer of condensed gases with very different properties from ordinary air, which forms part and parcel of the body, and constitutes a transition between genuine air on the one side and unmistakable copper on the other. This layer, or "Bunsen-schicht," is warmed directly by contact with the solid, and by molecular diffusion it warms the next outer layer, which, sending out quick-flying molecules, warms the next, and so on. Ultimately a stationary state is reached, and the temperature must fall continuously as we recede from the surface, according to some exponential law when convection-currents are permitted, but otherwise linearly.

The air-film next the solid is known to cling tightly to the solid, and not to be quickly removed. Its adherence need not, indeed, be one relating to individual molecules; it may be only a statistical one, but its renewal is known to be such a slow process that it is very unlikely that it appreciably streams upward even when fairly hot. The layer outside this streams upward a little, being retarded by viscosity or molecular diffusion as it shears itself over the inside layer. It in its turn retards the next, and so on, the velocity of upstreaming increasing as we go out from the surface. But this increase of velocity of successive layers only goes on to a certain limit; it soon reaches a maximum, because the temperature of the successive layers is rapidly decreasing, and thus they have less tendency to rise although there is now very little to prevent them, until at a distance from the solid the air is at rest.

There is, then, in all convection-currents from a vertical surface a layer whose velocity is a maximum; on either side of it the velocity is diminishing—on the cool side because the temperature gets less and less; on the hot side, in spite of the high temperature, because of the viscosity. The maximum-velocity layer marks the position of compromise between the lightening due to temperature and the resistance due to the neighbourhood of the solid.

The fact that the convective velocity increases and reaches a maximum as you recede from the solid, combined with the fact that the temperature constantly diminishes as you go in the same direction, seems to us to have an important bearing on the production of the dust-free space by molecular bombardment in a way we will endeavour to explain.

A mere steady fall or gradient of temperature as one recedes from a body will not of itself produce the differential bombardment necessary to keep back the dust-particles. For though it is true that the air is hotter on the side next the body than it is on the far side, this excess of temperature does not result in an excess of pressure but in a defect of density. The air near a warm body is less dense than the air outside, but it is not at a greater pressure; at least, if it is, it is a new phenomenon, and one not to be expected from any known action of a solid upon gas, except, of course, within the extremely minute range of the molecular forces estimated by Quincke at the five-millionth of a millimetre. The warm gas therefore would produce no greater bombardment on the one side of the particles than the cold gas produces on the other; for though each molecule hits harder and hits oftener, there are fewer molecules to hit; and the one effect compensates the other as soon as a stationary condition as to distribution of temperature has been attained. Not before; for so long as the air near a solid is getting warmer, there is a more rapid diffusion of molecules outward than there is inward, and till equilibrium is reached there will certainly be a pressure outwards from the body sufficient to drive the dust back.

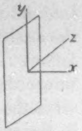
If the air near a solid can be kept stagnant while the body is warmed, the dust in it ought to be driven back at first by the outward heat-diffusion; but as soon as a stationary temperature-condition has been attained, this bombardment ought to cease, and permit the dust to slowly settle back again if it likes. This is much the case of the interior of a glass tube, and, we believe, explains the quick formation of a coat when the light is first turned on to any surface, and also the reason why such coats in stagnant air, though broad, are hazy and indefinite in outline.

But suppose the air near the body is rapidly changed (in the case of the tube by blowing through it, or by convection-currents in ordinary cases), the stationary state never is reached, the air outside the body is always getting warmed, and the bombardment may always continue. The function of the convection-currents, then, is to prevent the arrival of the stationary state, and so to perpetuate the dust-repelling bombardment, at the same time that they sweep off some of the already cleansed air and bring up dusty air at such a rate that the bombardment has as much as it can do to keep a layer clear. The coat therefore tends to become thinner when convection-currents increase; and if currents are unfairly produced (as by blowing), the coat may be swept away faster than it can be renewed, and so wholly disappear. But if excess of temperature only is the cause of the currents, then the same cause which strengthens them also assists the bombardment, and accordingly the coat is not swept off by such currents, but may even become thicker as the temperature rises. At the same time it is not to be expected that small differences of temperature will much affect the coat, because of the compensation action already explained. Moreover, we have at present no theoretical guarantee that a rise of temperature need thicken the coat; it might thin it in some media. All we can say is, that convection-currents have a double action, both helping the formation, and causing the removal, of the coat.

But now, how does the fact of an increasing upward velocity of the air as we go through successive layers from the surface of a body account for the differential bombardment or greater internal pressure necessary to account for the driving back of the dust? Without technicalities, we answer this question as follows:—Consider a vertical flat plate at a higher temperature than the air. We grant that the total pressure of the air is the same near a warm solid as it is anywhere else; that is, the average mean square of molecular velocity is simply proportional to the temperature; but then the average mean square of velocity can be resolved into three components—normal to the surface, parallel to the surface and horizontal, and parallel to the surface and vertical. If the air were at rest, all three components would be equal; but in any given layer the air is not at rest, it is up-streaming: consequently the vertical component of velocity is greater than the average, and so some other component must be less. The horizontal component of velocity parallel to the surface we naturally assume to be simply the average. The component normal to the surface must therefore be less than the average. In other words, though the total pressure is the same in all directions, its vertical component in the case of up- or down-streaming air is greater, and hence the normal component is less; and the amount by which the normal component of the pressure is less than the average at any given distance from the body depends upon the velocity of the convection-current at that place.

But the current-velocity increases as we go from the body to a maximum, and then decreases: consequently the normal component of the pressure, starting from its average value close to the surface, decreases as far as the maximum-velocity layer, where it reaches a minimum, and then increases. It is this differential normal pressure from the surface which the dust-particles feel, and they are driven back towards the maximum-velocity layer. They may not, indeed, be driven quite to it, because there must be a compromise between the rate at which dust is carried past the surface and the distance to which the differential bombardment has time to drive them through the air.

It is easy to see that any differential bombardment will be simply proportional to the volume of the particles, provided their thickness is small; hence the behaviour of big particles relatively to small ones will be like their settling behaviour under gravitation.



Putting the matter in symbols, let us call the plane of the solid yz, y being vertical; and let u, v, w be the three component velocities along x, y, z respectively, and T the absolute temperature; and let $=$ signify proportion only when convenient: then

$$u^2+v^2+w^2=3\,\mathrm{T}.$$

But at a distance x from the surface let the convection upstreaming velocity be ϕ, and let the velocity along z be the average: then

$$w^2=\mathrm{T},$$

and $$v^2=w^2+\phi^2;$$

so $$u^2=\mathrm{T}-\phi^2.$$

Hence u decreases as ϕ increases, and there is accordingly a bombardment up towards the maximum-velocity layer from either side.

Calling the three components of the pressure p_x, p_y p_z, it can be shown that

$$p_x=\rho u^2,$$

$$p_y=\rho v^2,$$

and $p_z=\rho w^2=p$, the proper pressure of the gas.

Hence $$p_x=\rho(\mathrm{T}-\phi^2)$$

$$=p-\rho\phi^2=p\left(1-\frac{\phi^2}{\mathrm{T}}\right);$$

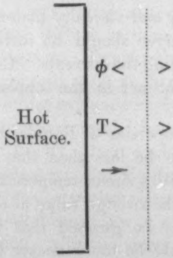
and $\frac{dp_x}{dx}$, which determines the intensity of the differential molecular bombardment per unit distance along the normal to the surface, is proportional to the original pressure and to the rate of change of $\frac{\phi^2}{T}$.

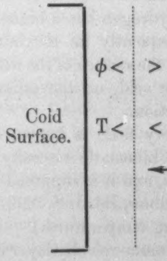
Remember that ϕ is the up-streaming velocity, and T the temperature, of the different layers. In a region where ϕ is increasing and T is decreasing, the differential bombardment is considerable, and it acts in the direction of increasing ϕ. In a region where ϕ and T are both increasing or both decreasing the bombardment is likely to be feeble, and may be *nil* if ϕ varies with the root of T.

Now outside a warm plate we have near the surface ϕ increasing and T decreasing as you go outwards : consequently here is an outward bombardment. Further on both are decreasing, so the bombardment is feeble or *nil*, and one cannot say without further consideration which way, if any, it ought to act.

Close to the surface of a cold body proceeding outwards ϕ is increasing, but T is also increasing : consequently there is here feeble bombardment. Further on ϕ is decreasing and T still increasing ; consequently here is a bombardment inward towards the body.

Representing these things diagrammatically, the arrow represents the direction of the bombardment when it is decided, the dotted line the maximum-velocity layers :—





Now, the conductivity of a gas for heat, and the viscosity which resists its own motion, are each of the nature of a diffusion or interchange of molecules; and, as shown in Maxwell's 'Heat,' the three things—the diffusivity, the conductivity, and the effective (or "kinematic") viscosity, are all proportional to one another, and vary directly with the square of the absolute temperature, and inversely as the pressure.

Returning to the warm solid, with its up-streaming air-currents and maximum-velocity layer towards which dust is bombarded from the surface, it is evident that a rise in the temperature of the solid would throw this layer further out from its surface (and so thicken the dust-free coat), both because the conductivity of the gas improves, and because its viscosity near the surface increases with temperature. A fall of temperature, on the other hand, would throw the maximum-velocity layer inwards, until, when the solid was colder than the air, the maximum down-streaming layer might be very close to the surface, because its viscosity would be least there, and because the conductivity of the gas would then be so poor. (N.B. We never assume that the dusty air is warmed by *radiation* from the solid, because the far more powerful electric-light radiation produces no particular effect on the dust except in the neighbourhood of bodies.) The effect of an increased pressure would be to diminish both the conductivity and the viscosity in the same proportion; and so for both reasons it would throw the maximum-velocity layer inwards, in fact it would act like cold. Rarefaction of the air would act like an increase of temperature.

Hydrogen has a higher conductivity and viscosity than air, consequently its maximum-velocity layer should be further from the surface of the warm solid exciting the currents. Carbonic acid, on the other hand, should act in the opposite direction.

Very little is known about the properties of liquids, but their kinematic viscosity is known to be less than that of gases, and it is supposed to decrease with a rise of temperature (Wüllner, Bd. I. S. 326, Flow of liquids through tubes at different temperatures). Hence it may be guessed that the maximum-velocity layer in liquids should be much nearer the surface of the solid causing the currents than in gases, and that a rise of temperature would bring it still nearer. On the other hand, it may be expected that cold would drive it further off the solid, so that any phenomena connected with this layer in liquids might be better developed in descending cold currents than in ascending warm ones.

In conclusion, the writers wish to call attention to a paper read to the Royal Society of Edinburgh, by Mr. John Aitken, on the 21st of January this year, and of which an abstract appeared in 'Nature' of the 31st January last. Judging from the abstract, it would appear that Mr. Aitken, so well known for his previous researches on dust-particles as nuclei, has been travelling over much of the same ground as we have, and that he has arrived on the whole at similar conclusions.

University College, Liverpool.

II. *On some Experiments illustrating an Explanation of* Hall's *Phenomenon. By* SHELFORD BIDWELL, *M.A., LL.B.*[*]

[Plate II.]

IN a recent communication to the Royal Society I attempted to show that the apparent action of a magnet upon an electric current (well known as Hall's Phenomenon) might be completely explained by the operation of mechanical strain and certain Peltier effects.

My experimental acquaintance with the subject began in July 1883, and I have since devoted a considerable amount of attention to it. But the paper referred to contained only a bald and simple statement of the results at which I finally arrived, little or nothing being added by way of comment or explanation. To my mind, saturated as it was with the matter, it appeared that such a statement afforded in itself overwhelming evidence in favour of the views which I had been led to adopt; and I believed that when once set forth, however briefly, they could not fail to meet with immediate acceptance. But Hall's own theory of the phenomenon has for some years been universally recognized as interpreting a well-established law of nature. It seemed to be in complete harmony with the views of Clerk Maxwell as to the existence

[*] Read March 8, 1884.

of a rotatory coefficient of resistance: it has provided a field for investigation to mathematicians of the highest eminence; and it has derived additional interest and importance from the fact that it was believed to point to an intimate relation between electricity and light. Under the circumstances, it is reasonable that such a theory should not be abandoned without the exercise of very considerable caution.

I propose therefore in this paper to treat the subject in greater detail than at first seemed necessary. Attention will be directed to facts and arguments which in my former paper were left altogether unnoticed; and those points which, as I have gathered from conversation and correspondence, seem to present the greatest difficulty, will be considered at some length. With regard to the experiments upon which I rely, such of them as are new are of a very simple character, and can easily be repeated by any one possessing a reflecting galvanometer. They are of course of a somewhat delicate nature, and more suitable for the laboratory than for public demonstration; but I shall be bold enough to attempt the performance of most of them in the presence of the members of the Physical Society.

Mr. Hall's first paper on the subject appeared in Silliman's Journal in 1879, and is reproduced in the 'Philosophical Magazine' for March 1880. After stating that his object was to prove that the current of electricity in a fixed conductor is acted upon by a magnet, he describes the following experiment:—A strip of gold-leaf, forming part of a circuit, was placed between the poles of an electromagnet, cutting the lines of force perpendicularly. The terminals of a galvanometer were applied to opposite edges of the gold-leaf, and moved about until two equipotential points were found. The magnet was then excited, and a galvanometer-deflection immediately occurred. This deflection was too large to be attributed to the direct action of the magnet upon the galvanometer-needle. It was permanent, and so not due to induction. It was reversed when the magnet was reversed. "In short," says Mr. Hall, "the phenomena observed were just such as we should expect to see if the electric current were pressed, but not moved, toward one side of the conductor. In regard to the direction of this pressure, as dependent on the direction of the current in the gold-leaf and the direction of the lines of magnetic force, the following statement may be made:—If we regard an electric current as a single stream flowing from the carbon pole of the battery through the circuit to the zinc pole, the phenomena indicate that two currents in the same direction tend to repel each other. But if we regard the current as a stream flowing from negative to positive, then the phenomena indicate that two currents in the same direction attract each other." The meaning of this is, as appears from subsequent papers, that the direction of the transverse current across the gold-leaf is opposite to that in which the gold-leaf itself would move across the lines of force if it were free to do so. If the two points to which the galvanometer is connected are joined by an equipotential line across the gold-leaf, the effect caused by magnetization may be expressed by saying that the equipotential line is rotated in a direction *opposite* to that of the current circulating in the coils of the electromagnet.

A second paper was published in the 'Philosophical Magazine' for November 1880, in which were described experiments made with other metals in addition to gold. With silver, nickel, tin, and platinum the direction of the transverse effect was the same as with gold, though it differed in degree in the case of every metal. But with iron the direction of the transverse current was found to be reversed; a fact which Mr. Hall was naturally inclined to attribute to the magnetic properties of that metal, though he was at a loss to account for the difference between its behaviour and that of nickel, which is also strongly magnetic. In iron, therefore, the equipotential lines are rotated in the *same* direction as that of the current circulating in the coils of the electromagnet.

In a third paper, published in the 'Philosophical Magazine' for September 1881, the author says that the direction of the transverse electromotive force in the magnetic metal cobalt was the same as in iron. In this paper it is stated that $\frac{E'}{V}$ is probably a constant for any given metal; E' being the transverse electromotive force per centimetre of the width of the strip, and V the direct current divided by the section of the conductor. This quantity $\frac{E'}{V}$ is called, in accordance with a suggestion of Dr. Hopkinson, the "rotational coefficient" of the metal. The direction of the transverse effect or sign of the rotational coefficient is in iron and metals which behave like iron called +, because its direction is that which the conductor itself bearing the current would follow if free to move across the lines of magnetic force. In gold and similar metals the sign of the rotational coefficient is called −.

A fourth paper appeared in the 'Philosophical Magazine' for May 1883, entitled "Rotational Coefficients of various Metals," in which it is stated that aluminium, copper, and brass behave in the same manner as gold, that zinc behaves like iron, and that with lead no transverse effect whatever is produced.

Collecting Mr. Hall's various results, we find that, of the thirteen different metals which he has tested, three (iron, cobalt, and zinc) are classed as positive; nine (gold, silver, tin, copper, brass, platinum, nickel, aluminium, and magnesium) are negative; and one (lead) shows no signs of rotation.

I began a repetition of Hall's experiments with the object, if possible, of carrying them further, and especially of establishing in a satisfactory manner the existence of a connexion between the phenomena in question and the magnetic rotation of the plane of polarized light. My earlier experiments were made with iron, of which I happened to possess a suitable specimen in the form of foil ·019 millim. thick. The magnet used consisted of a bar of soft iron, 38 millim. in diameter, bent into horseshoe shape; if pulled out straight its length would be about 50 centim. It was covered with about 600 turns of wire, 2 millim. in diameter; the pole-pieces used were 30 millim. square, with flat ends, and were generally fixed about 6 millim. apart. The magnet was excited by a battery of either seven Grove's or, more generally, of five 3-quart bichromate cells.

The arrangement of the apparatus is shown in fig. 1 (Plate II.), where P P′ is the strip of metal cemented to a plate of glass, and placed above one pole, S, of the electromagnet; M is a section of the yoke of the electromagnet; B is a battery of one or two cells, generating the current through the strip; C a commutator to reverse the direction of the current; B′ the electromagnet battery; C′ a commutator to reverse the magnetism; W W′ wires from equipotential points in the metallic strip to the galvanometer G; K a key in the galvanometer circuit.

The method of proceeding was as follows:—A current was passed from B through the strip P P′, and sliding-contacts on the opposite edges were adjusted until, when the key K was depressed, no deflection of the galvanometer occurred. The magnet was then excited by the battery B′, and on again depressing K the galvanometer was deflected. On reversing the direction of the current either from B or B′, by means of one of the commutators, an opposite deflection occurred when K was depressed. The galvanometer used was a reflecting instrument, of ·2 ohms resistance; it was placed at a distance of 4 metres from the scale, upon which it reflected the image of a very fine wire. The scale, key, and commutators were all within easy reach of the operator.

With this comparatively small apparatus there was at first some difficulty in producing a sensible Hall effect, and the greatest care had to be exercised to avoid disturbing influences. In addition to the possible sources of error mentioned by Mr. Hall, I was much troubled by one which he does not seem to have noticed, and which may probably account for the uncertain nature of some of his results. It was found that, though the galvanometer-deflection indicating the Hall effect was invariably reversed when the direction of the magnetizing current was reversed, it sometimes appeared to be altogether independent of the direction of the current passing through the strip. It occurred to me to excite the magnet without passing any current at all through the strip; and I found that when the key K was depressed a steady deflection of the galvanometer occurred, which was reversed on reversing the magnetizing current. That this effect was not due to the direct action of the magnet on the galvanometer-needle was proved by the fact that, when the key was raised, the deflection immediately ceased. It appeared at first sight as if the magnet had the power of generating a current in the strip of metal. But this, of course, was impossible if the magnetic force remained constant. I concluded therefore that it was an effect of induction caused by weakening of the magnet in consequence of the running-down of the battery, or perhaps of the resistance of the wires being increased by the heating-effect of the current; but it was difficult to see how this could induce a current in the strip which was symmetrically situated with regard to the lines of force. Finally, I found that the effect was produced, not in the strip at all, but in the wire which passed from the strip between the arms of the electro-magnet to the galvanometer. When this wire was led out on one side of the yoke, the deflection produced was opposite to that which occurred when the wire was led out on the other side; and if the wire was turned half a dozen times round the magnet, the resultant galvanometer-deflection was so great that the spot of light disappeared from the scale. This was ultimately remedied by forming the wire in question into a loop embracing the yoke of the magnet, as shown at L L′ (fig. 1). From this loop an independent wire W′, attached to a sliding binding-screw D, was led to the galvanometer. It was found that the position of D could be so adjusted that, K being steadily depressed, the magnetism of the electro-magnet might be interrupted, or even reversed, without causing any material deflection of the spot of light even at the instant of the change. When so adjusted it was, of course, impossible that the comparatively small changes in the magnetic force, caused either by polarization of the battery or by the heating of the wires, could have any effect upon the galvanometer. The Hall effect now came out with great distinctness, the deflections to the right or left of the zero-point of the scale, caused by exciting the magnet, being generally as much as 15 or 20 centim.*

A number of experiments were now made with pieces of iron cut into various shapes, and occasionally with fine copper wires arranged in different forms, and the conviction gradually forced itself upon me that the effect in question was not due to any such action of the magnet upon the current as that which Mr. Hall supposed.

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* That the magnetizing current used by Hall was not absolutely constant is evidenced by a statement in his paper in the 'Philosophical Magazine' for September 1881, that the readings of a tangent-galvanometer, placed in the circuit for a special purpose, "slowly decreased with the running-down of the current."

The possibility of a thermoelectric effect suggested itself at an early stage, the heat being derived from the current flowing through the strip, and the changes in direction being possibly produced by some effect of magnetization upon the thermoelectric properties of the metal. Such effects, I thought, could only occur at the points where the wires were attached which went to the galvanometer. Disks of bismuth and antimony were therefore inserted at the contacts of the wires and the strip, and their relative disposition varied in order that the thermoelectric effect, if any existed, might be exaggerated. But it was found that, whether the disks were of bismuth or of antimony, or of the two metals in various combinations, the extent of the galvanometer-deflections was unaffected, except in such a manner as could be perfectly accounted for by ordinary thermoelectric action. The idea of mechanical strain then occurred to me; and I may mention that this occurred to Mr. Hall, but only to be rejected by him as utterly inadequate to account for the phenomenon. I attached a string by means of sealing-wax across the middle of a thin sheet of iron, which was cemented to glass and connected with the battery and the galvanometer as usual. On pulling the string in a transverse direction I found unmistakable indications of a galvanometer-deflection in the same direction as if the sheet of iron had been acted upon, not by a mechanical pull, but by the electromagnetic force. The effect was small, but I have since greatly increased it by the following device:—A strip of thin iron was cemented between two thin slips of deal about 20 centim. long, forming a kind of sandwich. The sandwich was attached to a board by means of four screws, the distance between the middle screws being about 7 centim. The two ends of the iron were connected with a battery, and the middle points of its opposite edges with the galvanometer. On pressing with the finger the middle of one edge of the sandwich in a direction perpendicular to its length and in the plane of the metal, though no appreciable distortion was produced, the galvanometer was immediately deflected, the direction of the current from the strip to the galvanometer being always the same as the direction of the force. A similar sandwich was prepared in which platinum-foil was used instead of iron, and with this a transverse force produced opposite deflections to those which occurred in the case of iron.

There is, of course, no doubt whatever, as to the real existence of a mechanical stress in a conductor through which a current is passing, and which is at right angles to the lines of magnetic force. Its effect may be rendered evident to the eye by a simple experiment, to which I attach no importance whatever except as affording a rather pretty illustration of a perfectly well-known law. A shallow glass cell is fitted with iron electrodes at its two ends, and is filled with mercury to a depth of 3 or 4 millim. When this cell is placed between the poles of an electromagnet and a current is passed through it, the mercury along the transverse middle line is drawn towards one side of the cell. Here it is heaped up, and, yielding to the force of gravitation, it runs along the two ends of the cell in the opposite direction, once more to be urged forwards across the lines of force. The result of a continuation of this process is the formation of two little whirlpools of mercury which rotate in opposite directions in the two halves of the cell. The same effect may be produced, but with less violence, if a solution of sulphate of zinc is used with zinc electrodes.

Having completely satisfied myself that mechanical strain was concerned in the production of Hall's phenomenon, it remained to ascertain the *modus operandi.* Thermoelectric action again occurred to me, and I remembered that Sir William Thomson had discovered that thermoelectric effects occurred in stretched and unstretched wires of the same material when brought into contact with each other. On referring to Thomson's paper, which was published in the 'Philosophical Transactions' for 1856, I found it stated that if a stretched copper wire is connected with an unstretched copper wire and the junction heated, a thermoelectric current will flow from the stretched to the unstretched wire through the hot junction; while, if the wires are of iron, the direction of the current is from unstretched to stretched. There could be little doubt that effects of the same nature would occur in sheets of these metals; and I proceeded to consider the precise manner in which a sheet of metal conveying a current would be strained when placed between the poles of an electromagnet.

My first idea was that, since the magnetic force was strongest in the middle of the field, the lower half of the metallic sheet would be, on the whole, transversely compressed and the upper half extended. But I immediately saw that strains of this nature would not explain Hall's phenomenon, unless indeed it turned out to be the case that lateral compression and extension produced opposite thermoelectric effects to those caused by longitudinal compression and extension. The effect of lateral compression in an iron wire was noticed by Thomson in the paper referred to. He states that when an iron wire is laterally compressed, a current passes from uncompressed to compressed through the hot junction. He supposes therefore that since a lateral traction would probably produce the reverse effect of a lateral pressure, it would give rise to currents from stretched to free—the reverse of longitudinal traction. In making this experiment, Thomson used many turns of wire wound round a block of wood (to multiply the effect) and squeezed the whole in a hydraulic press. I attempted to repeat the experiment by a simple method and using only one wire; but no amount of pressure that I was able to produce resulted in any indication whatever of a current. I have since endeavoured to ascertain whether any appreciable current could be produced in a sheet of metal by lateral traction. The arrangement used is shown in Pl. II. fig. 2:—A B is a sheet of metallic foil; the shaded part D E was held between two fixed blocks of wood, and the shaded part C F between two blocks of wood which were attached to a lever. A heated glass rod was applied along C D, and on drawing the lever upwards in the direction of the arrow, a current immediately passed between the unstrained and the strained portions of the metal through the hot junction. Two metals only have been thus treated—zinc and iron; and the direction of the current was in both cases the same as if the traction had been longitudinal instead of lateral. In zinc the effect was very strong, in iron it was feeble, but not, I think, so feeble as to be doubtful.

On further consideration I came to the conclusion that no appreciable strains of the kind above referred to would be produced by the transverse force in the magnetic field. This force would be sensibly uniform across the whole of the middle portion of the strip, for the pole-pieces were flat and within a very short distance of each other, and the strip did not extend across their whole width. Considering the analogy of a beam of wood, rigidly fixed at both ends, and acted upon in the middle by a force perpendicular to its length, I imagined that the transverse force would tend to make the metallic strip assume a distorted form of the same character as that indicated in fig. 3. As thus distorted, the strip may be mapped out into six districts, in three of which the metal is, on the whole, subjected to longitudinal traction, while in the other three it undergoes compression. This, of course, supposes that the metal, though cemented to glass, is capable of yielding to some extent to the force acting upon it. And since neither the metal itself, nor the glass, nor the cement which connects them, is absolutely rigid, this must necessarily be the case, though probably in a very small degree. The ends C, D of the strip, which are in a weaker part of the magnetic field, or even removed from its influence altogether, will not be acted upon in the same manner; and if the strip is sufficiently long they will remain absolutely at right angles to the middle line, as shown in the figure. Two points of contrary flexure will therefore exist on each of the edges; and the necessary consequence of this will be alternate regions of compression and extension, as indicated in the figure. It seems to me that, however thin the metal may be, so long as it is not altogether without cohesion and elasticity, the action of a transverse force across the middle will affect it in some such manner as that pointed out, to some degree which may be very small.

I have prepared a rough model to illustrate my idea of the nature of the distortion which the plate undergoes. A number of narrow strips of deal are attached at short intervals to a rectangular sheet of indiarubber: they are equal in length, and parallel to the shorter sides of the rectangle. The two strips at the ends of the sheet are nailed firmly to a board; otherwise the indiarubber is free. If the middle strip of wood is drawn or pressed in a direction transverse to the rectangle, the indiarubber is distorted and assumes the form of fig. 3; and the regions which are there marked as stretched and compressed appear very clearly, the strips being drawn apart in the former, and crowded together in the latter. The same kind of distortion would be produced, though to a smaller extent, if the ends, instead of being rigidly fixed, were able to yield, more or less, to pressure or tension. But unless they were each attached to a single point, and were otherwise perfectly free (in which case the sheet would be longitudinally divided into two equal regions of compression and extension), some such distribution of strain as that indicated in fig. 3 must necessarily occur*.

Suppose now that a current is passing through the plate from C to D, and that A and B are two points on the opposite edges, which, when the metal is unstrained, are at the same potential. Then the ratio of the resistances between the points C and A, and the points A and D, is equal to that between the points C, B and the points B, D. And so far as mechanical strain alone is concerned, this equality will not be disturbed by placing the plate in a magnetic field, the strain produced being symmetrically distributed on both sides of the middle line. At all events, no strain could occur which would in itself affect the resistance of gold and iron in opposite ways, for the resistance of both is increased by extension, and (presumably) diminished by compression. But the currents from C to A and from B to D pass from regions which are compressed to regions which are stretched, while the opposite is the case with currents passing from C to B and from A to D. And here the thermoelectric effects come into play.

It has already been mentioned that a thermoelectric current will pass from a stretched copper wire to an unstretched copper wire in contact with it, if the junction is heated. From this it might be inferred, that a current would flow through the heated junction from an unstretched or free copper wire to a longitudinally compressed copper wire. And I have proved by actual experiment that this is the case. *A fortiori*, therefore, a current would pass through the heated junction from a stretched copper wire to a compressed copper wire. For similar reasons the current would, if the wires were of iron, flow in the opposite direction, from the compressed wire to the stretched wire, across the hot junction. And the same effects, so far as regards currents between stretched and unstretched portions, occur, as I have proved experimentally, if strips of foil are used instead of wires. If, therefore, a battery-current is passed from a stretched portion of a wire or foil to a compressed portion, heat will (according to the laws of the Peltier effect) be absorbed at the junction if the metal is copper, and will be developed at the junction if the metal is iron. In passing from compressed to stretched regions, the converse effects will occur.

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* It should be remarked that no account whatever is taken in the model of lateral compression and extension, which, as already stated, are probably very small in the case of the metallic sheets used in Hall's experiments.

Let us now imagine the metal plate to be divided into four equal regions A, B, C, D, as shown in fig. 4. Let a current pass through the plate from E to F, and let a force (produced electromagnetically or otherwise) be applied in the direction H G. First, suppose that the plate is of copper, then the current travelling from E to the line O G passes from a compressed to a stretched portion of the metal; heat will therefore be developed in the region A. Between the line O G and the point F, the current passes from a stretched to a compressed portion; heat will therefore be absorbed in the region B. For like reasons, heat will be absorbed in C and developed in D. The temperature of the copper plate will therefore not be uniform, the portions A and D being on the whole hotter than the portions B and C. But the resistance of a metal increases with its temperature. The resistance of A and D will therefore be greater, and the resistance of B and C smaller, than before the plate was strained. If therefore G H were originally an equipotential line, it is clear that it will be so no longer. An equipotential line through the point O will now be inclined to G H in the direction K L, as shown in the figure.

Supposing the plate to be of iron instead of copper, the Peltier effects will be reversed, and the regions which in the former case were hot will now be cold, and *vice versâ*. The distribution of resistance will be changed in a corresponding manner, and the equipotential line will be rotated in the opposite direction.

The peculiar thermoelectric properties of copper and iron, discovered by Sir William Thomson, are thus seen to be sufficient to account for Hall's phenomenon in the case of those metals. If the explanation which I have offered be the correct one, it is clear that Hall's "positive" metals, cobalt and zinc, should, when tested by Thomson's method, exhibit the same thermoelectric effects as iron; that his "negative" metals should behave thermoelectrically in the same manner as copper; and that lead might be expected to be thermoelectrically unaffected by strain. It became exceedingly interesting to ascertain if this was the case, and I therefore proceeded to repeat Thomson's experiment upon all the metals mentioned by Hall. In most cases at least two or three different specimens of the metal were used, and, except in the case of cobalt, the following simple method of operating was adopted.

A short piece of the wire or strip of the foil to be examined was held at the ends by two fixed brass clamps, about 5 or 6 centim. apart, which were connected with the terminals of a low resistance reflecting-galvanometer. A point near the middle of the metal was then gripped by a pair of pliers which had been previously heated, and one half of the wire was drawn taut, leaving the other half slack. A galvanometer-deflection immediately occurred, which ceased when the tension was discontinued. The process was then repeated, the pull being made in the opposite direction: this resulted in an opposite deflection of the galvanometer.

Upon first gripping the metals, especially the harder ones, it frequently happens that before beginning to pull a thermoelectric current is set up between different parts owing to local differences in physical condition, and these thermocurrents are sometimes so strong as to completely mask the effect produced by stretching. Their effect may be practically eliminated by giving a series of short pulls at regular intervals, corresponding with the periodic swing of the galvanometer. The results can thus be observed with perfect accuracy, but the method is not well suited for use before an audience on account of the difficulty of rendering evident the correspondence between the pulls and the consequent galvanometer-deflections. The hand and eye should, in fact, work together*.

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* The experiment was, however, successfully exhibited at the meeting. All Hall's metals were used except cobalt, which could not be obtained in the form of wire, and the only doubtful case was that of tin, the wire

The directions of the currents through the hot junctions are given in the following table, which is taken from my former paper, with the addition of the results for wires of tin and lead:—

S = Stretched. U = Unstretched.

Metals.	Forms used.	Direction of current.	Hall's effect.
Copper	Wire and foil; pure	S to U	—
Iron	Wire and sheet; annealed	U to S	+
Brass	Wire, commercial	S to U	—
Zinc	Wire and foil	U to S	+
Nickel	Wire	S to U	—
Platinum	Wire and foil	S to U	—
Gold	Foil, purity 99·9 per cent.	S to U	—
	Wire, commercially pure	*U to S*	
	Jewellers' 18 ct. wire and sheet	S to U	
	Jewellers' 15 ct. sheet	S to U	
Silver	Wire and foil	S to U	—
Aluminium	*Wire and foil, pure*	*U to S*	— ?
Cobalt	Rod; 8 mm. diameter	U to S	+
Magnesium	Ribbon	S to U	—
Tin	Foil and wire	S to U	—
Lead	Foil (assay) and wire	No current	Nil.

It will be seen that, in every case excepting that of aluminium and one out of five specimens of gold, there is perfect correspondence between the direction of the thermoelectric current and the sign of Hall's effect. With regard to the aluminium, a piece of the foil was mounted upon glass, and Hall's experiment performed with it. As was anticipated, the sign of the "rotational coefficient" was found to be + like that of iron, zinc, and cobalt. It is probable, therefore, that the specimen of aluminium with which Mr. Hall worked differed in some respect from that used by myself. The anomalous specimen of gold being in the form of wire, could not be submitted to the same test: it probably contains some disturbing impurity.

With regard to cobalt, since it could not be obtained in the

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being ruptured before any marked deflection was produced. It should be noticed that the temperature of the hot junction should not exceed about 100° C., otherwise, at least in the case of iron and nickel, different results may be obtained.

form either of wire or of sheet, it was necessary for the observation of the thermoelectric effect to treat it in a somewhat different manner from that previously described. A rod of the metal was held firmly by one end in a vice, and both ends were connected by wires with the terminals of the galvanometer. The middle of the rod was gripped with gas-tongs which had been made hot in a Bunsen flame, and stress was produced by twisting. It was found that, while the stress continued, a current passed from the strained to the free portion of the rod through the hot part. The direction of the current was the same whether the twist was clockwise or counterclockwise, and it ceased the moment the stress was discontinued. For the sake of comparison, a copper rod was treated in a similar manner, and the resulting current was in the reverse direction. For the purpose of this experiment, torsion is clearly equivalent to traction, both tending to draw asunder the molecules of the metal.

Some months ago, when experimenting with pieces of iron cut into different shapes, I tried the effect of making a longitudinal slit along the middle of the plate. The result was, that the Hall effect was considerably weakened even though a stronger current was used than before the slit was cut. In the light of subsequently acquired knowledge, I have varied the experiment thus :—A plate of iron was prepared as usual, but the galvanometer-wires, instead of being attached in the ordinary manner, were connected to points nearer to the middle of the plate than to the edges. When the magnet was excited, the ordinary Hall effect was found to occur, but it was somewhat weakened. Two longitudinal slits were then cut along the middle of the plate, a connecting piece about 4 millim. wide being left at the centre. A current from two bichromate cells was passed through the plate, and the positions of the galvanometer connexions were carefully adjusted, until, on depressing the key K (see fig. 5), not the smallest movement of the spot of light occurred. The electromagnet was then excited, the key was depressed, and the spot of light was deflected. The magnet-current was reversed, the key was again depressed, and there was again a deflection of the spot of light. And the directions of the deflections were in both cases *opposite* to those which occurred before the slits were cut in the plate. The amount of deflection thus produced was about 35 scale-divisions *.

Now it is quite clear that, if Hall's effect were due to the direct action of the magnet upon the current, it ought to occur in each of the two halves of the divided plate. The transverse current in the lower half would (supposing its direction to be upwards in the figure) pass from the point B to the metallic bridge at the centre, and the transverse current in the upper half would pass from the centre to the point A. Upon no conceivable hypothesis could the mere division of the plate have the effect of actually reversing any direct action which the magnet might exert upon the current.

The strain theory, however, explains the matter perfectly. Supposing a south pole to be beneath the plate, and the current through it to be flowing from left to right, then, before the cuts were made, the point A would be in a stretched district, and the point B in a compressed district (see fig. 3); and the resulting Peltier effects would cause the transverse current to flow in the direction A G B, fig. 5. But in consequence of the longitudinal cuts, the distribution of stress is altered. Instead of the whole plate, each half of it may now be mapped out into six areas which are differently strained, and the point A will now be in a compressed district, and B in a stretched district. The Peltier effects will therefore be reversed, and the transverse current will flow in the direction B G A. The existence of the central bridge does not prevent the new strain, because there is no shearing at points midway

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* The experiment as described is an exceedingly troublesome one, and no attempt was made to exhibit it at the meeting. The difficulty arises from the fact that, in order to show the effect with certainty, a very perfect balance must be obtained, and this alone generally occupies a great deal of time. But even when two exactly equipotential points have been found, it often happens that the mere reversal of the polarity of the magnet disturbs the adjustment of the galvanometer-contacts to such an extent that the effect cannot be observed: more time must therefore be consumed in readjusting the contacts before a successful experiment can be made. Believing this inconvenience to be due to small displacements resulting from the attractive action of the magnet upon the iron, I have since tried the experiment with gold-foil. This turns out to be a much more suitable metal for the purpose, rendering it possible to observe the effect with ease and certainty.

between the ends of the plate; and as regards transverse distortion, the central bridge merely forms a link between the upper and lower portions of the plate, which link shares their movement in the upward direction without impeding it. Thus the reversal of the Hall effect is easily and completely accounted for.

The 'Philosophical Magazine' for last January contains a translation of a paper by Prof. Righi, on Hall's Phenomenon. He uses three electrodes instead of four. The current enters or leaves by one, and leaves or enters by the other two. The two partial currents pass through a "Wiedemann's" (presumably a differential) galvanometer, and zero is obtained by the use of resistance-coils. On exciting the electromagnet a galvanometer-deflection occurs, indicating a current in the opposite direction to that named by Hall.

This also can be explained by strain and Peltier action. Let us suppose, as before, that the plate is of iron, and that the south pole is beneath it. Let a current enter the plate at A, fig. 6, and leave it at the two points D and E by the wires leading to the differential galvanometer G. The plate is divided into six strained regions exactly as in Hall's arrangement, those which are compressed being marked C, and those which are stretched S. But the neighbourhood of the upper electrode D will, in this case, be *heated*, because the current is passing from stretched to compressed: the resistance of the region will therefore be increased. Similarly the resistance of the metal in the neighbourhood of the lower electrode F will be diminished. Thus a greater quantity of electricity will pass by E than by D, and the galvanometer-deflection will be in the opposite direction to that which would have occurred if the connexions had been made in the middle of the plate, in the usual manner. Righi's experiment therefore confirms my explanation of the Hall effect.

The theory which I have ventured to submit seems to me capable of bearing any test which could reasonably be applied to it. Not only does it completely account for the phenomena described by Hall, but it explains anomalies and enables one to predict results. The chief point of difficulty lies in the strain. In conversation on the subject, I have found that, while it is readily admitted that a strain such as is described might well be produced in a piece of metal a millimetre in thickness, it is by no means so easy to conceive the possibility of a similar strain in a sheet the thickness of which does not exceed a hundredth or a thousandth of a millimetre. But let it be imagined that the thick piece of metal is divided into a hundred or a thousand independent layers, each of which is acted upon by a force equal to a hundredth or a thousandth part of that which acted upon the whole. Then it becomes evident that each individual stratum, including the bottom one, will be affected in precisely the same manner as the sum of them which constitutes the thick plate. Of course, if the film of metal is so exceedingly thin that its physical properties of cohesion and elasticity are impaired, we should expect the effects of extension and compression to be diminished. This is, in fact, the case with thin gold-leaf, not so much on account of its mere thinness as of the inequalities and irregularities necessarily existing in it; and accordingly we find it noted by Mr. Hall (Phil. Mag. November 1880, p. 312) that the transverse effect in gold-leaf appears to be *relatively* much smaller than the effect in strips of sensible thickness*. *Cæteris paribus*, the galvanometer-deflection is, of course, greater with a thin sheet than with a thick one, because the difference of potential at any two points in a thick sheet must always be comparatively small.

If it is objected that, since the plate is firmly cemented to glass, the distortion actually produced must be very small, it may be replied that the consequent effect is also very small, and that a distortion far too insignificant to be visible to the eye would be sufficient to produce it. The warmth communicated to the plate by lightly touching opposite corners of it with the fingers is capable of causing galvanometer-deflections many times as great as those produced by Peltier effects requiring three or four amperes of current for their production.

Lastly, it may be urged that the force available for producing the required strain is a very small one. This is undoubtedly true. But, apart from the fact that a very small force would be sufficient to cause a sensible strain in a very thin sheet of metal, it must be remembered that the force with which we are dealing acts in an exceedingly advantageous manner. It does not, like an external push or pull, act upon a single point or group of points in the sheet, but it exerts a perfectly independent action upon every individual molecule of the metal which is within the magnetic field, most powerfully in the middle, gradually falling off towards the ends. It acts, in short, in the most effective manner possible for the production of the strain.

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* Mr. Hall thinks that the apparent difference may be accounted for by the existence of a multitude of small holes in the thin leaf, by impurities in the gold, and by the difficulty of securing good contact with the electrodes.

Though it may not impossibly turn out, on further investigation, that the details of the action differ in some respects from those which I have suggested, I think no reasonable doubt can remain that Hall's phenomenon is simply a consequence of mechanical action combined with Peltier effects. And if it should be thought that I have, in this paper, brought forward a superfluity of argument in support of a proposition which, when once stated, appears almost self-evident, I can only say that, under the circumstances, and having regard to the great importance of the subject, it seemed desirable that it should receive the most thorough and exhaustive treatment possible.

III. *On the Adjustment of Resistance-Coils.* *By* Professor SILVANUS P. THOMPSON, *B.A., D.Sc., Univ. Coll. Bristol*[*].

1. ALTHOUGH the existing methods for the exact measurement of the electric resistance of a wire are simple, rapid, and reliable to a very high degree, there is not, so far as I am aware, any simple, rapid, and reliable method yet known of adjusting resistance-coils to their exact value, when some standard coil of known resistance is used for comparison. It is, of course, much more important to know what the exact value of a coil is than to have that coil adjusted to one ohm or one hundred ohms, if such adjustment involves some uncertainty in the percentage of its precise value. But I do not see why our standards should not only be accurately

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[*] Read February 23, 1884.

known, but also accurately adjusted to standard values, at least with far greater precision than is often the case. Further than this, the great cost of reliable resistance-coils, which hinders in many cases their being purchased by individuals and institutions of limited means, arises almost entirely from the high cost of the skilled labour now needed for the tedious processes of adjusting the coils by trial and error to something approaching their nominal values.

The method of adjusting resistance-coils now suggested has proved itself in practice far more accurate than any other, and the rapidity with which adjustment can be secured is extraordinary. It consists in taking as a first approximation a wire cut off roughly of such a length as to have a resistance slightly greater than that to be finally given, and then shunting the whole or a portion of this coil by a coil of much higher resistance, also approximately cut off to a resistance calculated from a single careful measurement of the first rough coil. The method, though new for the construction and adjustment of permanent coils, is not new as a method in general, as it was used nearly twenty years ago by the Committee on Electrical Standards for temporary adjustments. On page 101 of the Reports, as reprinted under the editorship of Prof. Fleeming Jenkin, the following passage occurs :—

"The idea of using large coils combined with small ones in multiple arc to obtain extremely small minute differences of resistance was suggested to the writer by Professor [now Sir] W. Thomson, and will be found useful in very many ways." But only one way is mentioned in the Reports, namely that of plugging in the high resistance as a temporary shunt during a single experiment.

2. I will first describe the method pursued in the Physical Laboratory of University College, Bristol, for the adjustment of coils not exceeding 10 ohms in resistance. First, the length, calculated to within 0·5 of a centimetre, is cut off from a specimen of German-silver wire of which the resistance per centimetre is roughly known; 2 per cent. being added before the wire is cut off. It is soldered to the stout copper terminals prepared to receive it, doubled on itself, twisted, wound up, and when the soldering has cooled, the resistance of the wire

is measured with the utmost care by comparison, made on Professor Carey Foster's method, with a standard coil, constructed at Cambridge in Professor Stuart's workshops, and which has been verified at the Cavendish Laboratory and certified in terms of Lord Rayleigh's determination of the ohm. The "rough resistance" of the measured coil being thus very accurately known, a calculation is made to ascertain what resistance, connected as a shunt, will reduce the resistance between terminals to one exact Rayleigh ohm. The resistance required for the shunt is in practice from 12 to 50, 60, or even 80 ohms. The nearer the first approximation, the higher the shunt-resistance required, as the formula given below shows at a glance. The calculation then having been made, the requisite length to approximate to this is cut off from a much finer wire, which is then soldered across the terminals. At first we used to measure the resistance of these shunts before putting them on. In practice we find this quite unnecessary, as they can always, if there is any error of importance, be readjusted after soldering them to the copper terminals. In nine cases out of ten, however, no further adjustment is needed.

3. The following is the theory of, and formula for, the value of the shunt required.

Let $\mathfrak{R}$ be the exact resistance of the first rough approximately-cut coil, being larger by from 1 to 4 per cent. than the final value. It is required to find the value S of a shunt-coil which will reduce its resistance to the final exact value R.

By the ordinary rule for divided circuits we have

$$R = \frac{\mathfrak{R}S}{\mathfrak{R}+S},$$

$$R(\mathfrak{R}+S) = \mathfrak{R}S;$$

whence

$$\frac{\mathfrak{R}R}{\mathfrak{R}-R} = S.$$

4. An example for the adjustment of a 1-ohm coil will illustrate the method and its advantages. The following data are taken from the note-book of Mr. C. C. Starling, Demonstrator in the Physical Laboratory of University College, Bristol, January 30, 1884. Coil marked "ϕ 3."

1·1 metre of German-silver wire (No. 24 B.W.G.), diam. 0·56 millim., cut off and soldered to terminals. Tested (by Foster's method) against Cambridge Unit No. 6.

$$\mathfrak{R}=1·0385518 \text{ (temp. } 17°·2 \text{ C.)}$$

$$\frac{1·0385518}{·0385518}=33·9 \text{ ohms required as shunt.}$$

7·05 metres of German-silver wire (No. 36 B.W.G.), diam. 0·2 millim. (at 20·8 centim. per ohm), cut off, and without further measurement soldered to terminals. *Immediately* tested by Foster's method,

$$R=1·007912 \text{ Rayleigh ohms (temp. } 17°·3 \text{ C.).}$$

Time required to make and test coil and shunt 38 *minutes.*

This coil was tested again three days later, namely on February 3, and gave

$$R=1·004178 \text{ (temp. } 13°·5 \text{ C.).}$$

Tested again, February 5,

$$R=1·0050854 \text{ (temp. } 14°·5 \text{ C.).}$$

Tested again, February 21,

$$R=1·0063923 \text{ (temp. } 15°·5 \text{ C.).}$$

This coil is therefore correct at 0°·97 C.

One other example of the application of the method to a bad case will suffice. In this instance the resistance of the main wire was not near enough to the final value, being more than 14 per cent. too great, and the shunt consequently shorter than desirable. Nevertheless the result was quite satisfactory.

One-ohm coil made in Physical Laboratory, University College, Bristol, by Mr. C. Swan,

$$\mathfrak{R}=1·14599.$$

Shunt required 7·85 ohms. Cut off and soldered. Final testing by Foster's method, as follows :—

$U=0·9890385$ *Rayleigh ohms.* (This is the standard "Cambridge Unit" verified at the Cavendish Laboratory.)

$x'=68·845$ (mean of three readings).

$x\ =65·280$ " " "

$\mu =$ 0·0031 ohm per centimetre of the bridge wire.
$R = U - \mu(x - x')$.
R = 1·0000900 *Rayleigh ohms* (temp. 16° C.).

[Tested again next day this same coil gave
R = 1·0000435 *Rayleigh ohms* (temp. 17°·2 C.).]

5. The amount of the final error caused by any given error in the shunt is easily expressed by a formula. Let r be the error of the shunt, and n the ratio of the shunt to the unshunted resistance. In practice $60 > n > 10$. If the shunt S were without error we should have, from the usual formula,

$$R = \frac{\mathfrak{R}S}{\mathfrak{R} + S};$$

or, if S were truly equal to $n\mathfrak{R}$,

$$R = \frac{n\mathfrak{R}}{1 + n}.$$

But in reality $S = n\mathfrak{R} + r$, and consequently the shunted coil has for its slightly erroneous final resistance,

$$R' = \frac{\mathfrak{R}(n\mathfrak{R} + r)}{\mathfrak{R} + n\mathfrak{R} + r}$$

$$= \frac{n\mathfrak{R} + r}{1 + n + \frac{r}{\mathfrak{R}}}.$$

Therefore we get as the final error,

$$\epsilon = R' - R = \frac{r}{(n+1)^2 + \frac{r}{\mathfrak{R}}(n-1)}.$$

The second term in the denominator is always small compared with the first term, and may be omitted, for n is never less than 10, as remarked above, and r is very seldom one fiftieth part of $\mathfrak{R}$, and need not, with care, exceed one two-hundredth. This reduces the expression for the error to

$$\epsilon = \frac{r}{(n+1)^2}.$$

Suppose the error r made in measuring the shunt is as much as 2 per cent., and the value of the shunt-ratio n only 10; then, as the formula shows, the final error is only ·0165 per cent., or in a 1-ohm coil amounts to 0·000165 ohm. But if, as is in practice much more frequently the case, the shunt-ratio *n* is 50 instead of 10 (and often more), then with a 2-per-cent. error in the shunt the final error is only ·000767, or in a 1-ohm coil amounts to 0·00000767 ohm. In practice, the error made in cutting off the shunt wire is nothing like 2 per cent.: one half per cent is easily attainable.

6. The special advantages possessed by this method of adjustment cease to be available for resistances exceeding 10 ohms, as it is not convenient to measure off shunts of 500 to 800 ohms; for the wire is either inordinately long, or too thin for a reliable proportion to exist between length and resistance. For resistances exceeding 10 ohms we therefore modify the process of adjustment as follows. The wire is roughly measured out as before, to a value slightly exceeding the final correct resistance. It is soldered to the usual stout copper terminals; but before it is doubled, twisted, and wound up, a spot is bared at about one tenth or less of its length from one end. At this point a short piece of copper, about 2 millim. thick and 3 centim. long, is soldered. The resistance of the whole wire is then very accurately measured by Foster's method, and the resistance of the short portion between the terminal and the copper piece is also very accurately measured. We next calculate the value to which the resistance of this short piece must be reduced in order to bring the total resistance to its correct desired value, and then the short portion is shunted down to the required amount by a shunt-wire calculated, measured out, and soldered on, exactly as described before.

7. In conclusion, I would remark that in advancing from coils of 1-ohm to coils of higher values we have followed the suggestion made by Lord Rayleigh in 1881, of passing by three threes plus one to ten, and three thirties plus ten to one hundred. We have, however, found it much more convenient not to use the ingenious but complicated system of mercury-cups suggested by Lord Rayleigh for facilitating this operation. Instead of this we have employed the following simpler device. Six holes are drilled in a block of paraffin for mercury-cups. The holes have sheet-copper disks fixed at the bottom. Each cup is large enough to admit of the insertion of three stout copper terminals. Figures 1 and 2 below show how the

arrangements are made for connecting the three threes in parallel, for verification, and for connecting the three threes plus one in series, when using them for testing a 10-ohm coil. In both figures the letter *c* denotes a connecting bar of stout copper.

Fig. 1.

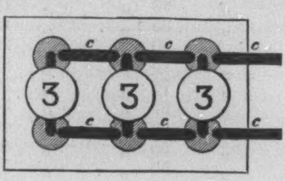
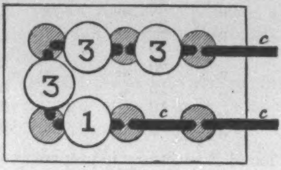


Fig. 2.



My thanks are due to my assistant, Mr. Colman C. Starling, Demonstrator in Physics in University College, Bristol, for having zealously aided me in working out the methods of adjustment described above.

IV. *Note on the Electric Conductivity and other Properties of the Copper-Antimony Alloys.* *By* GEORGE KAMENSKY, *Assoc. Royal School of Mines**.

It is remarkable that the physical constants of the alloys of copper and antimony have hitherto been but little examined, more especially as the series is a very striking one; and the so-called "Regulus of Venus," which was well known to the alchemists, stands out prominently, with its beautiful violet colouring, both from the rest of the copper-antimony series and from the alloys of other metals.

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* Read June 23, 1883.

As a typical set to work upon I selected the following series :—

No.	1.	Antimony	100	parts.	Copper	0	parts.
,,	2.	,,	95	,,	,,	5	,,
,,	3.	,,	90	,,	,,	10	,,
,,	4.	,,	85	,,	,,	15	,,
,,	5.	,,	80	,,	,,	20	,,
,,	6.	,,	75	,,	,,	25	,,
,,	7.	,,	70	,,	,,	30	,,
,,	8.	,,	65	,,	,,	35	,,
,,	9.	,,	60	,,	,,	40	,,
,,	10.	,,	55	,,	,,	45	,,
,,	11.	,,	50	,,	,,	50	,,
,,	12.	,,	45	,,	,,	55	,,
,,	13.	,,	40	,,	,,	60	,,
,,	14.	,,	35	,,	,,	65	,,
,,	15.	,,	30	,,	,,	70	,,
,,	16.	,,	25	,,	,,	75	,,
,,	17.	,,	20	,,	,,	80	,,
,,	18.	,,	15	,,	,,	85	,,
,,	19.	,,	10	,,	,,	90	,,
,,	20.	,,	5	,,	,,	95	,,

I afterwards found it necessary to prepare two more, viz.:— No. 10*a*, Antimony 49, Copper 51, which has the formula $Cu_2 Sb$; and No. 13*a*, Antimony 31·9, Copper 68·1, which possesses the formula $Cu_4 Sb$.

From the point of view of the metallurgist, the most interesting fact connected with the electrical constants of the alloys is the determination of the group to which, following Matthiesen's classifications*, they belong. Are the alloys of copper and antimony like, for instance, those of copper and tin, "solidified solutions of one metal in the allotropic modification of the other"; and if so, is the curve of their electrical resistance a *continuous* one, showing at first a rapid fall on the copper side, and then turning and passing nearly horizontal to the point representing unalloyed antimony?

The entire series of the copper-antimony alloys is unfortunately very brittle, and therefore the preparation of wires is out of the question, and the determination of the electrical resistance of cast rods of metal is known to be attended with many difficulties. I therefore determined to follow the course indicated by Prof. W. Chandler Roberts[*], who has shown that the necessary information as to the electrical position of alloys may be readily ascertained by the induction-balance; and the accuracy of his view was subsequently confirmed by Dr. Oliver Lodge[†], who used the Wheatstone bridge. The method adopted in the case of the induction-balance consists in placing the disk to be examined on one side of the balance, and in superposing a graduated wedge-shaped scale of zinc over the opposing coil. This method has already been described by Prof. Roberts[‡], who has lent me the graduated zinc scale by which his numbers representing the "induction-balance effect" of various alloys were made.

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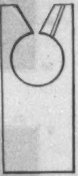
* Phil. Trans. British Association Reports, 1863.

It is true that the numbers named by the use of this scale are arbitrary; but they can be controlled by employing disks of pure metal of known resistance, provided that they have the same dimensions and volume as the disks of the alloys under examination.

The alloys were cast direct into the required disks, which was managed by using an ingot-mould in which a steel plate cut out, as here shown, was inserted. The disks so cast were ground down on a stone to a thickness of 3 centim.



In mapping out the curve of Electric Conductivity, I decided, after consultation with Prof. C. Roberts, not to give the number obtained for the disk of copper, as in his opinion that cannot be determined for a disk of the same size as the rest of the series by the particular zinc scale used.

I here give the readings obtained with the balance:—

No. 1.	58	No. 11.	85
,, 2.	69	,, 12.	57
,, 3.	74·5	,, 13.	52
,, 4.	77	,, 13*a*.	48
,, 5.	87	,, 14.	53
,, 6.	89	,, 15.	60
,, 7.		,, 16.	63
,, 8.	105·5	,, 17.	65
,, 9.	120	,, 18.	77
,, 10*a*.	121		

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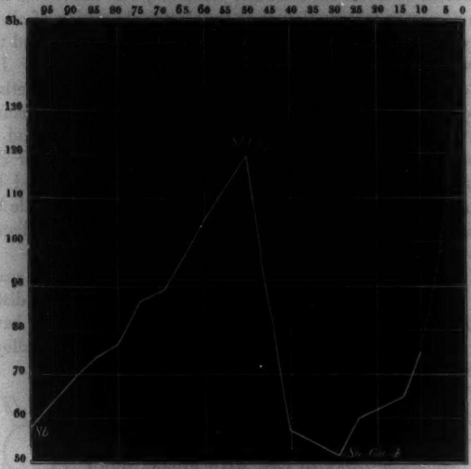
[*] Phil. Mag. July 1879.

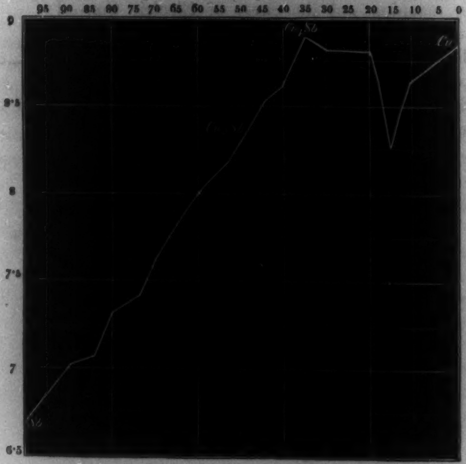
[†] Phil. Mag. February 1880.

[‡] *Loc. cit.*

Curve of Electric Conductivity.



Specific-Gravity Curve.



It will be seen that the curve, viewed as a whole, is of the ∠ shape, which Matthiesen found to be characteristic of the class of alloys of which the copper-tin series is the type. There is a very rapid fall from copper to the alloy containing only 15 per cent. of antimony; and this decrement is continued until the alloy $SbCu_4$ is reached, when the curve turns rapidly and rises to $SbCu_2$, and then turns again and passes to pure antimony. It is not a little interesting that, in the copper-tin series (Roberts), the alloy $SnCu_4$ occupies the lowest part of the curve, precisely the position that, in the copper-antimony series, is occupied by the alloy $SbCu_4$. In the copper-tin series, however, the second critical point is held by the $SnCu_3$; and this point in the copper-antimony curve is assumed, *not* by $SbCu_3$, but by $SbCu_2$.

I may add that I have confirmed the composition of the alloys at these critical points by analysis.

	$SbCu_2$.		$SbCu_4$.	
	Analysis.	Theory.	Analysis.	Theory.
Copper	50·85	50·5	68·38	68.1
Antimony ...	49·15	49·5	31·62	31·9
	100·00	100·0	100·00	100·0

In determining the specific gravities, I find that they rise gradually and evenly from antimony to the alloy Cu_4Sb (whose specific gravity is 8·871), and then diminish to the specific gravity of copper. The "Regulus of Venus" has a specific gravity 8·339, which does not in any way stand out from the rest.

Sb.	Cu.		Specific gravities.
100	0	....	6·700
95	5	....	
90	10	....	7·005
85	15	....	7·080
80	20	....	7·306
75	25	....	7·407
70	30	....	7·615
65	35	....	
60	40	....	7·995
55	45	....	8·194
50	50	(Cu_2Sb)	8·339
45	55	....	8·504

Sb.	Cu.		Specific gravities.
40	60		8·617
35	65	$(Cu_4 Sb)$	8·871
30	70		8·823
25	75		8·811
20	80		8·802
15	85		8·262
10	90		8·637
5	95		8·727
0	100		8·85

The following is a description of the fractures of the series:—

No. 1.		Bright white, highly crystalline.
„ 2.		Dull white, highly crystalline.
„ 3.		Grey, highly crystalline.
„ 4.		Grey, finely crystalline.
„ 5.		Dull fibrous, crystalline.
„ 6.		Bright purplish, highly crystalline, more than No. 1.
„ 7.	Very brittle.	Bright purplish, large plates of crystal.
„ 8.		Bright purplish, smaller plates of crystal.
„ 9.		Bluish, very finely cryptoconchoidal.
„ 10.		Purple, fibrous.
„ 11.		Purplish grey, fibrous.
„ 12.		Bluish grey, conchoidal.
„ 13.		White vitreous, fine granular.
„ 14.		Yellowish white, fine granular.
„ 15.		White, extremely fine granular.
„ 16.		Grey, granular.
„ 17.		Reddish grey, granular.
„ 18.		Orange, coarse granular.
„ 19.		Light red, granular.

The alloys from Nos. 12 to 16 are easily tarnished.

From this it will be seen that antimony is very persistent in its influence, and also that the colour of the "Regulus of Venus" first appears in the alloy containing 75 per cent. of antimony, and disappears in that containing 45 per cent.

From these data it would appear that in the copper-antimony series there are two alloys which may be assumed to possess very definite compositions—viz. the "Regulus of Venus," $SbCu_2$, and the alloy represented by the formula $SbCu_4$.

V. *Direct-Reading Electro-Measuring Instruments, and a Non-Sparking Key.* *By* Professors W. E. Ayrton, *F.R.S., and* John Perry, *M.E.*[*]

[Plate III.]

The construction and use of our various measuring-instruments are now so sufficiently well known that it is unnecessary for us to give any general description of them; indeed the names "Ammeter," "Voltmeter," by which we ventured to christen two of our children, have found favour in the eyes of Electricians, and are now current in electrical literature as the typical names, or surnames, of instruments used to measure strong currents and large electromotive forces respectively. But just as improvements in electrical measurements have led, step by step, to the names for the electrical units receiving more and more exact definitions, so we now propose to take advantage of certain important improvements that we have recently effected in our measuring-instruments to define the names "Ammeter," "Voltmeter," and "Ohmmeter" more exactly.

Proportional Law.—In the earliest form of instruments commercially employed for measuring the large currents used for electric lighting, viz. the instruments of M. Deprez, reference had to be made to a table of values to ascertain the meaning of any particular deflection, since there was no immediate connexion between 1 degree deflection and 1 ampere; and, further, it was necessary to refer to the table twice over when measuring two different currents, as the deflections were not proportional to the current. By giving a proper shape, however, to the coil, needle, and pole-pieces of the controlling permanent magnet, we succeeded (in 1880) in producing instruments in which the current or potential difference was exactly proportional to the deflection throughout the whole range of the scale; and, further, by the employment of our commutator principle an instrument was obtained having two degrees of sensibility, one exactly ten times the other; so that a commutator ammeter, or voltmeter, although employed to measure strong electric currents and large potential differences respectively, could be calibrated by the employment of a single cell of known electromotive force but of totally unknown resistance.

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[*] Read January 26, 1884.

Objections to the Employment of a Constant.—But these instruments possessed one serious fault looked at from the user's point of view, and two others which especially concerned the manufacturer. The scales of all the instruments were divided into degrees; and although the deflections were proportional respectively to the current or the potential difference to be measured, still there was nothing to show to how many amperes or volts one degree of the scale corresponded. Consequently for each instrument there was a "Calibration Constant," such as 1·75 ampere or 2·14 volts per degree, which was determined experimentally by the makers. We have here two of such old type of voltmeter, in one of which 5·7 volts produce one degree deflection, and in the other 0·09 volt produces one degree; the former being intended for measuring electromotive forces up to about 250 volts, the other the electromotive force of a single cell. But the employment of such a constant had the very serious objection that, as all the instruments looked exactly alike, there was the great danger in any factory, where several of these instruments were in use, of the constant for one instrument being used accidentally for that of another. And this mistake not only renders the answer, of course, quite wrong, but is liable to lead to the destruction of the instrument, or at any rate to the breaking of the pointer, from, say, an instrument having a constant 0·12 ampere per degree being put on a circuit through which 50 amperes are flowing, in consequence of the experimenter mistaking the "constant" for 1·2 ampere per degree. Further, even if no mistake be made in the "constant," it is troublesome, except for those who are expert in mental calculation (a quality not always predominating in the men in the charge of electric-light circuits), to multiply a "constant" 3·17 by the deflection, say 21·32, quickly without the employment of paper and pencil.

We therefore decided, not merely to avoid using tables of values such as had to be employed by M. Deprez, but even to abandon the use of constants altogether, and to arrange matters so that the pointer pointed at once throughout the whole range of the scale to the number of amperes or volts to be measured; to design, in fact, "Direct-Reading" instruments. And for the future we propose to confine the definition of an "Ammeter," a "Voltmeter," and an "Ohmmeter" to instruments on which respectively amperes, volts, and ohms can be immediately read off without any calculation or any reference to a constant or table of values.

On the table there are various specimens of our new Direct-Reading Ammeters and Voltmeters. In each case the dial is a complete disk (see Plate III. fig. 1), and not a sector as in the old instrument. The light aluminium pointer is also much longer, and the length of the graduated arc over which its end moves is much greater, so that readings with the new instruments can be made much more accurately than in the old. Here is a direct-reading ammeter suitable for measuring up to 10 amperes, correct to a tenth of an ampere; here another for measuring up to 150 amperes, each division of the scale corresponding with one ampere. I now send a current with these accumulators through this thick German-silver wire, and you see at once from the deflection on this ammeter, without any reference to a table of values, and without the employment of any troublesome constant, that the current passing, and which is now making the wire white-hot, is 207 amperes. Again, each division on the scale of this voltmeter corresponds with 1 volt, this particular instrument being suitable for measurements up to 100 volts.

To construct a direct-reading instrument it is necessary to employ some form of adjustment for sensibility, since to have a special scale engraved for each instrument after it was wound would be both troublesome and expensive; and, further, if there were no power of adjustment, any change in the strength of the permanent controlling magnet would prevent the instrument from any longer giving one division-deflection per ampere or per volt—in other words, would necessitate the employment of a constant.

Difficulties of Manufacture of Older Forms.—As regards the two defects from the manufacturer's point of view they were these:—Even although the shape of the coil, needle, and pole-pieces of the magnets were made accurately to templates, it was found difficult, when very thick wire had to be coiled on the bobbin of an instrument for measuring strong currents, to wind it with certainty so that both the deflection was proportional to the current, and that equal deflections on the two sides of the zero had exactly the same value. As long as the wire was thin, symmetry of winding was comparatively easy to obtain; but when thick wires, having but a few convolutions, were wound round a small bobbin, the thickness of the wire, combined with the galvanometric importance of each of the few convolutions, especially of those closest to the needle, made it necessary to wind and rewind some of the instruments several times before the proportional law, as well as equal deflections right and left, could be obtained.

Adjustment of Direct-Reading Instruments.—It therefore was important, to avoid complexity of construction, that the adjustment for sensibility referred to above should, if possible, be so contrived as to serve also for an adjustment for the proportional law. And this we are happy to say we have at last succeeded in accomplishing, by fitting into each end of the bobbin round which the wire is wound specially constructed charcoal-iron cores fitted with a fine screw. If these cores be too far out or out altogether, the proportional law will probably not be true, the current increasing more rapidly than the deflection; on the other hand, if they be screwed fully home the proportional law will also not be true, the deflection now increasing more rapidly than the current; but we find that between two limiting positions of these iron cores the proportional law is true; and by moving the cores in or out within these limits, the sensibility of the instrument can be much altered without destroying the proportional law.

To construct then, say, a 50-ampere instrument, wire is selected of such thickness, first, that 50 amperes will not heat it too much; secondly, that a sufficient number of convolutions can be wound on the bobbin for 50 amperes to deflect the needle to the limit of the scale when it is controlled by a permanent magnet of normal power. A scale divided for 50 amperes (that is, having the division marked 50 amperes at the end of its range) is then put on, and the soft-iron cores screwed in or out a little by trial until the pointer is found to point to exactly the same number on the dial as the number of amperes of current flowing through the coil. If at any time it be found that the permanent magnet has lost some of its magnetism, so that less than, say, 40 amperes will deflect the pointer to 40 amperes on the dial, the iron cores are unscrewed out a very small distance until the change in the magnetism of the controlling magnet is exactly compensated for.

The other adjustment to be employed by the makers for equalizing the deflections right and left for the same current is effected by fixing the coil so that it can turn about its centre.

The "Ten Law" of our commutator-instruments, which means that an ammeter is exactly ten times as sensitive when the commutator is turned to series as when to parallel, while a voltmeter is ten times as sensitive when the commutator is turned to parallel as when turned to series, is effected by the ten wires forming the bobbin having, inclusive of the resistance of the contacts at their ends, exactly the same resistance; which condition being fulfilled, it is quite unnecessary for obtaining the ten-law that the ten wires composing the strand should be at all symmetrical in the way in which they are wound on the bobbin. With some of our earlier commutator-instruments the resistance of the contact of the springs with the metallic pieces of the commutator introduced an error when the ten wires were each thick and short, since then the terminal resistance was a very material portion of the whole resistance of any one of the ten wires. To avoid this the commutators and the springs, as will be seen from the various specimens of the instruments on the table, which, Darwinian-like, show the history of the survival of the fittest, have assumed a much larger form.

In our direct-reading commutator-instruments the scale is double, as may be seen from fig. 2; the upper numbers corresponding with the number of volts when the commutator is to parallel, the lower when to series; while in a Direct-Reading Commutator Ammeter the upper numbers correspond with the number of amperes when the commutator is to series, and the lower when to parallel.

Fig. 3 shows the interior of the latest form. A A is the bobbin round which the wire is coiled; M M is the permanent controlling magnet, made in two parts to obtain considerable strength; P P are the soft-iron pole-pieces of special shape, to be referred to further on; F F are the soft-iron cores, and B B is a connecting bridge-piece of charcoal-iron used in our latest form of instrument for increasing the strength of the deflecting field for a given current by connecting magnetically these iron cores together. This addition is very important in voltmeters; since, although in an ammeter the constant of the instrument is nearly independent of temperature, this is not the case in a voltmeter. The current producing a given deflection in either instrument is practically independent of temperature; but the potential difference necessary to be maintained at the terminals of the instrument to produce the current, and which potential difference is what the voltmeter is designed to measure, depends necessarily on the resistance and therefore on the temperature of the coil. A temperature-correction can be easily made for the portion of the effect arising from the temperature of the room; but the unknown amount of heating of the coil arising from the passage of the current is far more difficult to allow for. Hence it is generally necessary to be contented with a weaker controlling permanent magnet for a voltmeter in order that the magnetic effect necessary to produce any given deflection, and consequently the heating effect which is proportional to the square of this magnetic effect, shall be less in the case of a voltmeter than in an ammeter. But the employment of our soft-iron pole-pieces combined with the soft-iron bridge enables us to use much more powerful controlling magnets, and therefore to obtain a much greater dead-beatness, and a greater freedom from disturbance produced by extraneous powerful magnets with our last form of voltmeters than with our earliest.

German-Silver or Copper Wire for the Coil of a Voltmeter.— It might appear at first sight that German-silver wire would be better than copper wire for voltmeters. As regards the error arising from the change of temperature of the room this is undoubtedly the case, but not as regards the heating of the coils by the passage of the current. For, to produce any given deflection on a voltmeter provided with a given controlling permanent magnet requires a given current for a given number of convolutions; hence, since the specific resistance of German silver is about 13 times that of copper, the production of heat, which necessarily accompanies the production of a given magnetic effect with a given instrument, will be 13 times as great if German silver be used than if copper be used. And on account of the inferior heat-conducting power of the German silver the elevation of temperature will be probably more than 13 times as great. But for the same elevation of temperature the increase of resistance of copper is only 8·8 times the increase of resistance of German silver. Consequently copper wire will be decidedly better than German-silver in any case where the change of resistance due to the heating produced by a current flowing through a given coil is concerned.

The question whether all the wire should be wound on the bobbin of the voltmeter, or whether a portion only should be on the bobbin, and the remainder of the resistance, necessary to be employed to prevent the voltmeter shunting too much of the main current, should be in the form of a resistance-coil, must be answered by the consideration as to whether the total consumption of energy which takes place when a particular deflection is maintained in the voltmeter, or the variation, arising from the heating of the bobbin, of the reading for a fixed potential difference, is the more important.

If it is desired that a particular deflection of the needle shall be maintained with the *least* total consumption of energy, then all the wire should be wound on the bobbin of the voltmeter; whereas if the heating-error is to be reduced to a minimum, then a large portion of the total resistance in the voltmeter circuit should be external to the voltmeter itself, and should be in the form of a resistance-coil made of German-silver wire, of sufficient thickness that its resistance is not sensibly increased when the current necessary to deflect the pointer of the voltmeter to the limit of its scale is maintained.

Methods of Construction for obtaining the Proportional Law.—Next, with reference to the principle that must be followed to obtain the proportional law in galvanometers. In an ordinary galvanometer controlled by the earth-magnetism, the strength of the controlling field is a uniform one; whereas the strength of the deflecting field produced by the current flowing round the coil is strongest in the plane of the coil, and grows weaker as we recede from that plane. Hence, when the needle is deflected, it moves into a weaker part of the deflecting field. The result of this is that the deflections for different currents increase much less rapidly than the current. If both fields be uniform for all positions of the needle, and be at right angles to one another when the needle is in its zero position, then, as is well known, the tangent of the deflection increases proportionately to the current. In order, then, that the deflection may increase proportionately with the current, one of three conditions must be fulfilled:—(1) the needle when deflected must move into a stronger part of the deflecting-field, or (2) must move into a weaker part of the controlling-field, or (3) both these results must be true. The first condition (uniformity of controlling-field combined with increase of strength of deflecting-field) can be fulfilled by using two solenoids at a small distance apart from one another, but with a common axis, and suspending the needle between them so that, on being deflected, it enters the solenoids and therefore moves into a stronger part of the solenoid field; or it may be fulfilled by a plan carried out practically by two of our assistants, Messrs. Walmsley and Mather, and which consists in suspending a magnet over two coils, C C, wound as shown by the dotted lines in fig. 4, the distance between the coils being rather less than the length of the needle.

This latter mode has been employed in our laboratory for making students' rough galvanometers, a specimen of which you see in its embryo state on the table, and with which the deflections are accurately proportional to the current at any rate up to 45° or 50°. If, however, a dead-beat instrument is required, then, in order to ensure roughly uniformity of controlling-field, the pole-pieces, P P, of the permanent magnet, M M, must be hollowed out, as shown in fig. 5, and must embrace the tube, T, in which the needle moves. We have made a number of ammeters and voltmeters of this type, and a sample one dissected is on the table. The augmentation of strength of the deflecting-field is still further produced by the employment of the soft-iron cores F F referred to above, and which screw into the brass bobbin A A.

But the condition 3 (the needle moving into a stronger part of the deflecting-field and also into a weaker part of the controlling-field) is the one we find the best, and it is the one we are using in all our latest experiments, the interior of one of which is shown in fig. 3.

Change of Strength of the Controlling-Magnet.—In some of our instruments we have found that the constant did not suffer sensible change during a period of many months; in others that the change during a much less time, arising from the falling-off of the strength of the controlling-magnet, was very serious. This latter effect we believe to be partly due to inferiority in the steel, it being very difficult to obtain successive deliveries of magnet-steel from the same manufacturer equally good in quality; and partly from the way in which the armature, attached to the instrument when not in use, was removed from the magnet when about to be used. In some of our older instruments, from the form of construction, the mode of removal of the armature took rather the form of a pull, which is known to be bad for the permanency of a magnet. Consequently our new Non-Commutator Instruments are so arranged as to make it impossible to use armatures at all, while in our Commutator Instruments armatures are attached; but the instrument is so constructed that the armature A (fig. 2) can only be removed by a pure sliding motion; and we shall thus be able to ascertain experimentally whether no armature at all, or an armature put on and removed by a pure sliding action, is the better for keeping the controlling-magnet constant in its strength. We anticipate, however, that no armature at all will be the preferable plan.

Ohmmeters.

An ohmmeter, as we have already said, we define to be an instrument in which the pointer points at once to the number of ohms required to be measured. The method we employ for making such an instrument consists in fixing two coils, at right angles to one another, acting on the same soft-iron needle. One of these coils, having terminals T T (Pl. III. fig. 6), is made of thick wire, and is placed in series with the resistance to be measured; while the other, having terminals *t t*, is composed of very fine wire, and is put as a shunt to the unknown resistance. Hence the main current produces its effect by means of the thick wire coil, and the difference of potentials at the terminals of the unknown resistance on the fine wire coil. Now by properly proportioning the shapes of coils, and by winding these coils in a definite way, we have obtained an instrument in which the deflection of the pointer is exactly proportional to the number of ohms, and which we find most convenient for measuring the resistance of any parts of an electric-light circuit; such as the field-magnet of a dynamo, or the resistance of an arc-lamp while the strong current is flowing. The thick coil is always kept, like an ammeter, in the main circuit, and the terminals *t t* of the fine wire coil are attached to any two points, the resistance between which, at any particular moment, it is desired to know. The use of this instrument also permits the employment of an iron wire, or even of a bit of wet rope, as a resistance-coil for experimental purposes, the resistance of the iron wire or of the wet rope being determined with the ohmmeter at the moment the experiment is being made.

Sir William Thomson has recently proposed a new unit, a "Mho," the reciprocal of an ohm, on account of the difficulty which is found in making people realize that one thousandth of an ohm may be of great importance when you are dealing with a large current. But we do not propose graduating our ohmmeters as mhometers, an operation of course quite simple to effect; because, first, if it be found that practical men cannot be got to pay attention to a thousandth of an ohm, we venture to think that they can probably be got to appreciate its value if it be called a thousand microhms; just as practical men do not disregard the capacity of a mile of submarine cable when called, as it always is, a third of a microfarad, although, possibly, they might do so if it were spoken of as a three millionth of a farad; and, secondly, a still greater objection to the adoption of the word "mho," ingenious as is this suggestion of Sir William Thomson's (like all his other suggestions), is that the constants in connexion with conductivity, the reciprocal of resistance, are quite different from those connected with resistance. For example, take the case of increase of resistance with temperature. Let R be the resistance of a wire at a temperature t° C., and R_0 that at 0° C.; then

$$R = R_0(1 + at),$$

where a is the increase of resistance per ohm per degree. Now let C and C_0 be the respective conductivities; then

$$C = C_0(1 - a't),$$

where a' is the decrease per unit of conductivity per degree of temperature.

But since $$R=\frac{1}{C},$$

$$\text{and } R_0=\frac{1}{C_0},$$

$$\therefore\ 1+at=\frac{1}{1-a't}.$$

When $a\,t$ and $a't$ are small, as in German silver, the percentage increase of resistance per degree equals the percentage decrement in conductivity per degree; but if $a\,t$ is large, as in copper, this is not the case; so that while ·388 is the percentage increase of resistance of copper per degree, ·293 is the percentage decrement of conductivity per degree.

Non-sparking Key.—Various so-called non-sparking keys have been devised during the last year or two; but, as far as we are aware, they by no means completely fulfil their object. On breaking a circuit through which a currrent is flowing, a spark is produced the brilliancy of which depends on the coefficient of seif-induction of the circuit, and on the current flowing through the circuit just before the circuit was broken. To completely avoid this spark, the energy stored up in the circuit must be utilized to send a current through an unbroken circuit, and this can be accomplished if the resistance of the circuit, instead of being suddenly varied from a small value to infinity, is increased steadily by the insertion of a resistance increasing at a proper rate. If it increases too quickly, a spark will certainly take place; if too slowly, the wire of the resistance-coil which has been added to the circuit will be dangerously heated.

Fig. 7 (Plate III.) shows an arrangement which we have devised for introducing this resistance at a proper rate, *independently* of any control on the part of the person stopping the current. To start the current, the handle H is turned moderately quickly until a solid piece of metal comes into contact with the brush B, when a catch holds the key in that position, and which is the position shown in the figure. The current now passes from one of the binding-screws to the other through practically no resistance. To stop the current the little handle, h, is slightly pulled, when a spring, S, which was coiled up when the handle was turned round to put the current on, causes the cylinder to turn in the opposite direction, the various metallic pins on the right-hand side coming, in succession, into contact with the brush B, until finally the pins M made of ebonite, and not of brass, come into contact with the brush B, and the circuit is entirely broken. Between each of the metallic contact-pins there is a resistance varying from a small fraction of an ohm for the first coil to some hundreds of ohms for the last. The effect is, then, that resistance at a *perfectly definite* rate is added to the circuit before breaking it.

These resistances are adjusted partly by calculation and partly by trial; so that with the particular rate of rotation which the coiled spring S gives to the barrel of the key, the circuit of an A Gramme machine sending a fairly strong current can be broken by the use of this key without any visible spark.

The spring S, combined with the locking-arrangement, makes it impossible for the key to be left partly on or off. If not put so that the current flows without resistance, then the spring S breaks the circuit altogether.

Besides the advantage this key affords of being able to break an entire electric-light circuit without spark, it is possible that another advantage may be produced, viz. that the life of incandescent lamps may be increased by the current passing through them being always gradually diminished to nothing, instead of being stopped as is at present the common practice; but whether this second advantage exists, which, however, seems extremely probable, time of course alone can prove.

At any rate the existence of a Non-Sparking Key now makes it possible for Insurance Companies to turn their attention to the question of prohibiting sparking altogether, which hitherto it has been almost useless contemplating.

VI. *On a Practical Point in connexion with the Comparison of Resistances.* *By* W. N. SHAW, M.A., *Emmanuel College, Cambridge**.

[Plate IV.]

THE most accurate method at present in use for the comparison of two resistances differing only by a small fraction of an ohm, is that suggested by Prof. Carey Foster (Journal Soc. Tel. Engineers, 1872). It is a method peculiarly suitable for the comparison of standards of resistance and the determination of temperature-coefficients of coils. It gives the difference of two resistances compared, free from errors, which might arise in the ordinary sliding-wire Wheatstone-bridge arrangement, from uncertainties as to the contacts of the ends of the slide-wire, or from the resistance of the connecting-pieces between the ends of the slide-wire and the electrodes of the coils compared. In the process of making a determination by this method, the two coils X and Y have to be made to interchange their positions, with reference to the other resistances of the bridge ; and it therefore becomes important for the application of the method that the observer should be able to interchange the connexions of the two coils with rapidity and facility.

This is very efficiently and conveniently provided for in the modified form of the slide-wire bridge devised by Dr. Fleming, and described in the third volume of the Proceedings of the Physical Society (p. 174)†. With the ordinary form of bridge the interchange is more difficult, for the coils to be compared have generally to be kept in water, and the two pairs of binding-screws of the bridge are a considerable distance apart, and thus the shifting of the coils to change their connexions is a somewhat inconvenient matter.

At the meeting of the Physical Society on Feb. 23, Prof. S. P. Thompson made some suggestions as to the manner in which the ordinary slide-wire bridge might be adapted so that Carey Foster's method could be conveniently applied.

We have, during the past three years, at the Cavendish Laboratory frequently had occasion to make use of the ordinary bridge for comparing coils and determining temperature-coefficients; and have accordingly found it necessary to devise some simple arrangement by which the easy and rapid interchange of the resistances under comparison could be provided for.

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* Read March 8, 1884.

† Phil. Mag. [5] vol. ix. p. 109.

I. A simple plan of securing the facility of interchange of contacts is to arrange four mercury-cups in a row, as 1, 2, 3, 4 in fig. 1, and connect them, as shown in the figure, with the binding-screws A B and C D of the bridge by stout copper rods. The mercury-cups should have thick copper bottoms, or, if the arrangement is to be permanent, may be formed conveniently of short bars of copper surmounted by pieces of india-rubber tube, so that connecting-rods can then be permanently fixed to the copper bars. The electrodes of the coils X and Y are inserted at 1 and 3, and 2 and 4 respectively, or *vice versâ*, and their connexions can accordingly be interchanged with very little motion. The electrodes can be kept in contact with the bottoms of the mercury-cups by elastic bands.

This plan of adapting the bridge differs but little from that described by Prof. Thompson, but is, perhaps, somewhat simpler.

II. The second method which we have been in the habit of using requires a more elaborate apparatus, but has the advantage that the contacts of the electrodes of the coils themselves are not altered during an experiment, the interchange being effected by means of a key. The coils under examination can, indeed, be soldered to projecting parts of the key if necessary, and the requisite contacts are secured by springs pressing down metal tongues into mercury-cups. The advantage of this arrangement is very considerable when experiments are being made by observers who are unfamiliar with the eccentricities of contacts.

The arrangement of the key is shown in plan in fig. 2, and in section in fig. 3. Eight mercury-cups 1, 2, 3, 4, 5, 6, 7, 8 are formed by boring holes in an ebonite plate, about half an inch thick, and screwing copper plates on the back (shown by dotted lines in the figure). These copper plates, which are carefully insulated from each other, connect the eight mercury-cups in pairs, and are brought out in tongues A, B, C, D, to which rods, forming connexions with the binding-screws of the bridge, can be soldered, or temporary contacts can be made by means of the mercury-cups formed by drilling the ebonite, as shown in the figure.

To another plate of ebonite, fixed opposite to these cups on the same board, four pairs of thick tongues of copper—I, II, III, IV, V, VI, VII, VIII—are attached, the ends of the tongues forming springs about 6 inches long. At the end of each spring a copper plunger is arranged to dip down to the bottom of the corresponding mercury-cup, into which it is pressed by a spring, S, as shown in fig. 3. The springs work against the crosspiece of wood M, M, and are insulated from the tongues by india-rubber.

A quadruple crank, Q, is arranged to be rotated between the supports of the crosspiece M, M by means of the handle H. The crank is put under the tongues at the points where they are pressed by the springs. By rotating this crank four alternate plungers (I, III, V, VII) are lifted out of their mercury-cups, the other four (II, IV, VI, VIII) being pressed in by the springs; or, on turning the crank through 180°, the four tongues (II, IV, VI, VIII) are lifted out and the other four pressed into contact by their springs.

The electrodes of the resistances to be compared are introduced into the mercury-cups α, β and γ, δ respectively, or they could be soldered to continuations of the tongues with which these cups are connected.

Thus rotating the crank determines one of the following series of connexions:—

1st position.	Contacts......	1 I.	3 III.	5 V.	7 VII.
	Connexions	A α.	B β.	C γ.	D δ.
2nd position.	Contacts......	2 II.	4 IV.	6 VI.	8 VIII.
	Connexions	A δ.	B γ.	C β.	D α.

So that the coils X and Y are alternately connected with A B and C D, and *vice versâ*, by a half-rotation of the crank.

It is necessary that any method of interchanging the coils should not alter the resistance of the connexions. It will be seen that the arrangement described is quite symmetrical, and therefore satisfactory in this respect, except for the piece of copper connecting I, II with δ; and the resistance of this, if the copper be fairly thick, is too small to be appreciable.

Cavendish Laboratory, Cambridge,
March 7, 1884.

VII. *Note on* Hall's *Phenomenon.*

By HERBERT TOMLINSON, *B.A.*[*]

IN a paper entitled "The Influence of Stress and Strain on the Action of Physical Forces"[†], I drew attention to the fact that there is a marked resemblance between the table of "rotational coefficients" drawn up Prof. Hall and that laid down by myself from the results of experiments on the effects of mechanical stress on the specific electrical resistance of metals. A comparison of the two tables given below shows that, with the exception of platinum, the metals stand in nearly the same order in both, and that iron and nickel are very conspicuous, the one at the top and the other at the bottom of the lists. The last-named metal is especially worthy of notice, because in it longitudinal traction, when not carried beyond a certain limit, diminishes the electrical resistance in spite of the increase of length and diminution of section which ensues.

Name of Metal.	Rotational coefficient[‡].	Temporary alteration of specific resistance per unit produced by temporary increase of length per unit. + signifies increase of resistance on application of stress.
Iron	+ 78·0	+2·618
Zinc	+ 15·0	+2·113
Tin	− 0·2	+1·630
Lead	0	+1·613
Platinum	− 2·4	+2·239
Silver	− 8·6	+1·617
Copper	− 10·0	+1·005
Aluminium	− 50·0	−0·420
Nickel..............	−120·0	−8·860

It might then be suspected that the results obtained by Hall are capable of receiving an explanation, in the fact that the electrical resistance of the strips of metal used by him would be altered by the mechanical strain consequent on their endeavour to move across the lines of magnetic force. Mr. Shelford Bidwell has, however, in his recent interesting communications to the Royal Society and the Physical Society, pointed out that "Hall's phenomenon" cannot be thus accounted for. Nevertheless, as it seems not improbable that there is some indirect connexion between the alteration of electrical resistance produced by mechanical stress and the "Hall effect," I have little doubt but that experiments on the "rotational coefficient" of nickel, in which the temperature is varied up to 100° C., or in which the strips are subjected to mechanical traction of varied amount, would assist in deciding the question as to whether purely mechanical stresses are to be regarded as producing the phenomenon. For it has been shown* that with this metal the maximum diminution of resistance following from longitudinal traction is at 100° C. *less than one half* of that at 15°; and, further†, that whilst traction not exceeding a certain limit produces diminution of resistance, increase of stress beyond this limit is followed by increase of resistance. Hall has remarked, in the 'Philosophical Magazine' for September 1881, that the transverse current obtained with a nickel strip is much *increased*, other conditions remaining unchanged, by rise of temperature. But his experiments in this direction are, I think, hardly conclusive; and, indeed, an examination of the numbers given in the column in which the values of the "rotational coefficient" are recorded shows, in the first *ten out of the eighteen* experiments, evidence that rise of temperature causes a *decrease* of the transverse current. Should Hall's phenomenon prove to result from mechanical strain, I incline to the belief that a rise of temperature from 15° to 100° C. will produce decrease in the transverse current.

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[*] Read March 22, 1884.

[†] Phil. Trans. Part I. 1883, p. 168.

[‡] A + sign attached to a metal signifies that the effect is in a direction the same as that which the conductor itself bearing the current would follow if free to move across the lines of magnetic force under the action of the ordinary "ponderomotive" force.

The experiments of Mr. Bidwell tend very largely to prove that the "Hall effect" can be explained by the joint action of mechanical strain and certain "Peltier effects." Should this be so, we ought, I think, to be able, by means of two thermo-elements connected with each other and with a delicate galvanometer, one element being in a cooled region and the other in a heated region, to put this theory to the test. Or, again, we might cover the strip with some material of bad thermal conductivity and watch for a gradual increase of transverse current with time when the electromagnet is excited, and gradual decrease when the electromagnetic stress is removed. Indeed in the actual arrangement adopted by Hall and Bidwell, it would seem that this gradual increase or decrease should occur; for though the strips themselves would rapidly cool if unmounted and exposed to the air, the nonconducting material of the mounting would take some little time both to gain and lose the heat imparted to it by the strip.

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* *Loc. cit.* p. 125.

† *Loc. cit.*

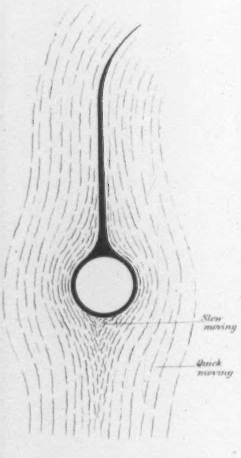

Slow moving
Quick moving

Fig 1.

Fig. 1a.

Fig. 3

Fig. 4.

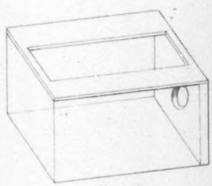


Fig. 5.

Fig. 6.

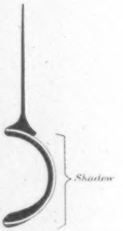


Fig. 2.

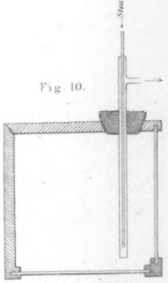


Fig. 10.

Sectional Plan.

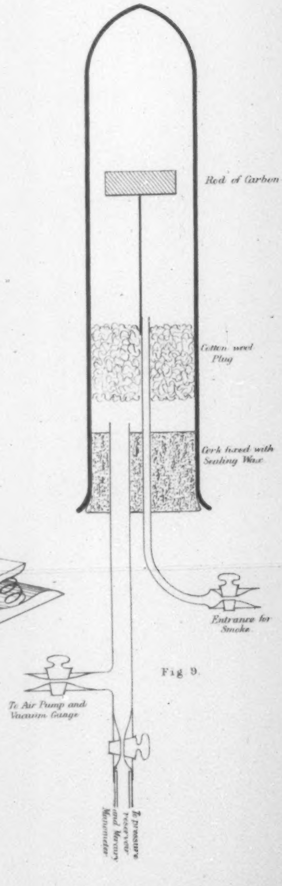
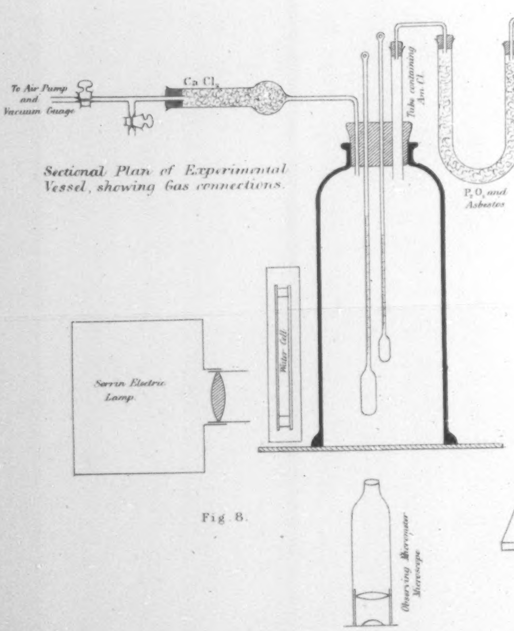
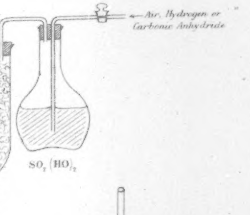

Rod of Carbon
Cotton wool Plug
Cork faced with Sealing Wax
Entrance for Smoke
To Air Pump and Vacuum Gauge
To pressure reservoir and Mercury Manometer

Fig 9.



To Air Pump and Vacuum Gauge
Ca Cl$_2$
Tube containing Am Cl
P$_2$O$_5$ and Asbestos
SO$_2$(HO)$_2$
Air, Hydrogen or Carbonic Anhydride
Water Cell
Serrin Electric Lamp
Observing Micrometer Microscope

Sectional Plan of Experimental Vessel, showing Gas connections.

Fig 8.

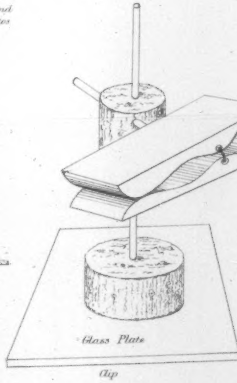

Glass Plate
Clip

Fig 7.

Mintern Bros imp

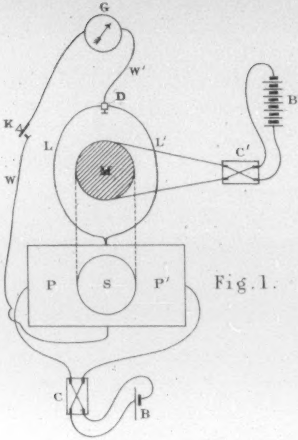

G
W'
D
B'
K
L
L'
C'
M
W
P
S
P'
C
B

Fig. 1.

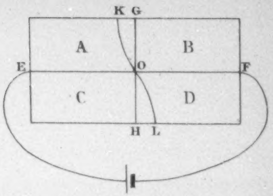

K
G
A
B
E
O
F
C
D
H
L

Fig. 4.

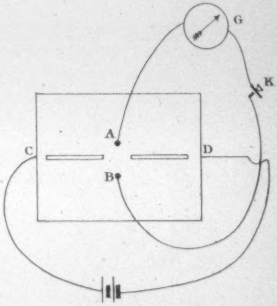


Fig. 5.

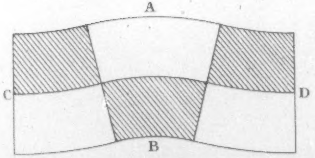


Fig. 3.

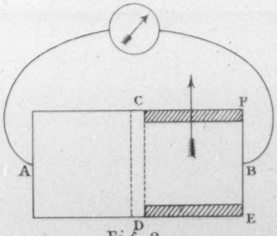


Fig. 2.

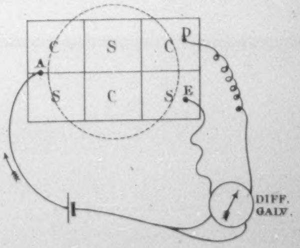

C
S
C
D
A
S
C
S
E
DIFF.
GALV.

Fig. 6.

Mintern Bros. lith.

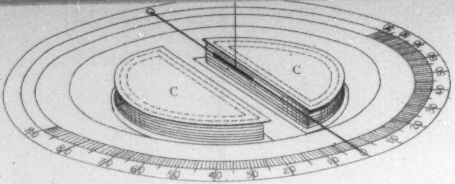

C
C
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90

Fig. 4.

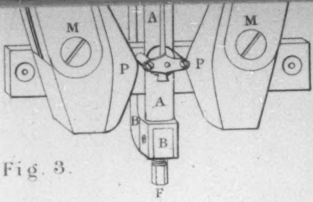


Fig. 3.

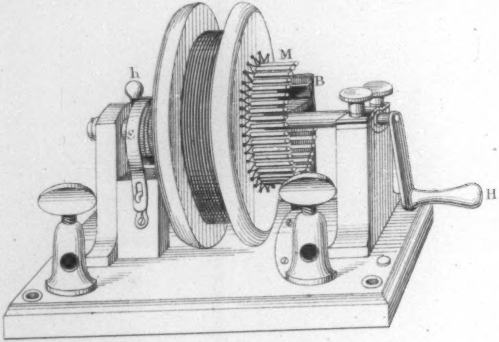


Fig. 7.

Minturn Bros lith

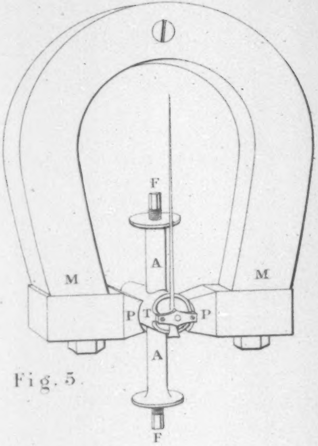


Fig. 5.

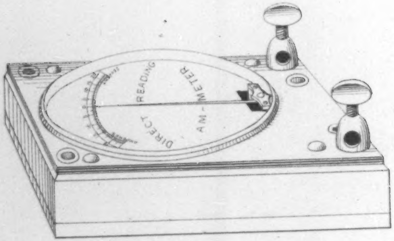

DIRECT READING
AM-METER

Fig. 1.

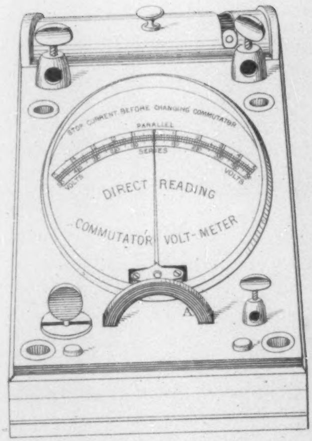

STOP CURRENT BEFORE CHANGING COMMUTATOR
PARALLEL
SERIES
VOLTS
VOLTS
DIRECT READING
COMMUTATOR VOLT-METER
A

Fig. 2.

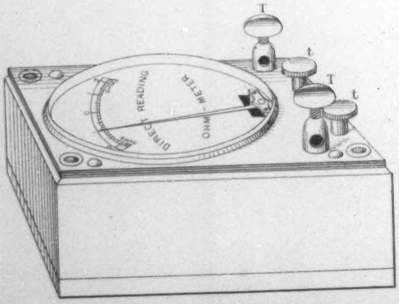
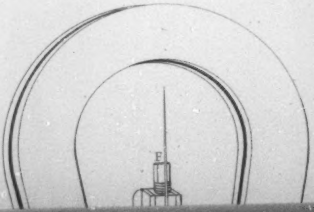

T
t
T
t
DIRECT READING
OHM-METER

Fig. 6.



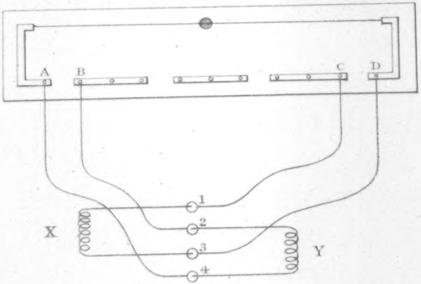
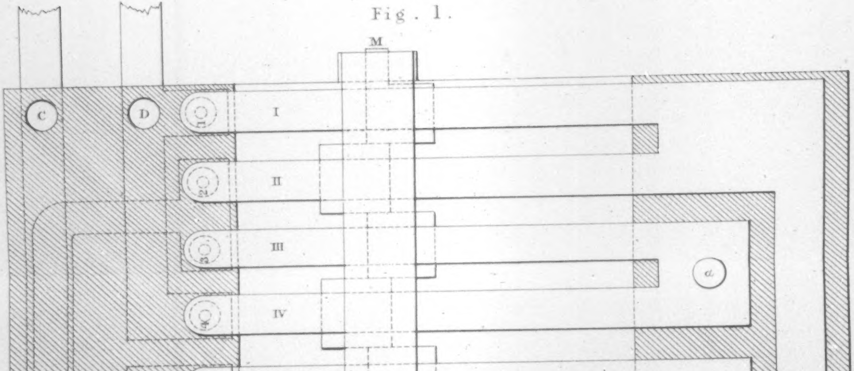

A
B
C
D
X
Y
1
2
3
4

Fig. 1.


M
C
D
I
II
III
IV
1
2
3
4
a

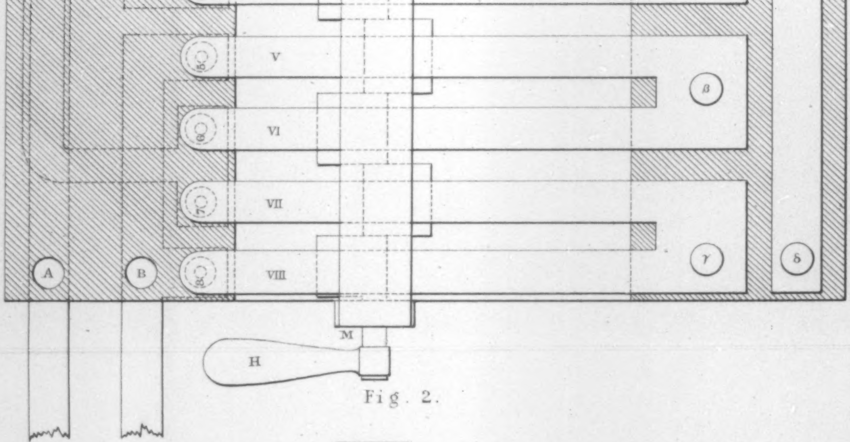

V
VI
VII
VIII
5
6
7
8
A
B
β
γ
δ
M
H

Fig. 2.

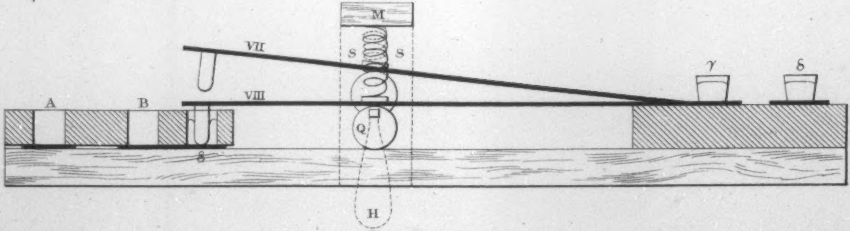
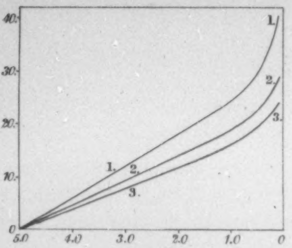

M
S
S
VII
VIII
A
B
S
Q
H
γ
δ

Fig. 3.

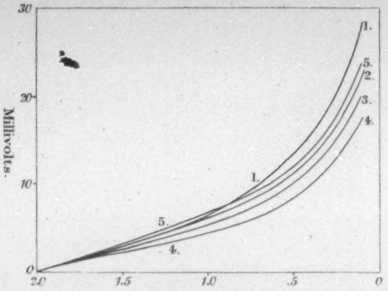
Mintern Bros. lith.

Fig. 1.



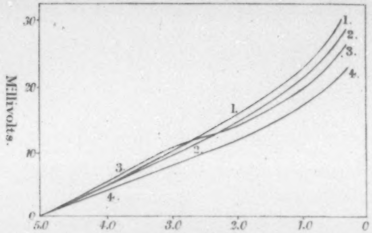
Zinc Sulphate.

Fig. 2.



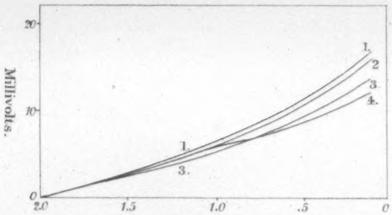
Copper Sulphate.

Fig. 3.



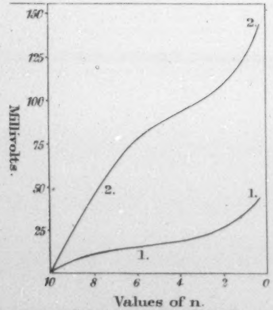
Cadmium Sulphate.

Fig. 4.



Cadmium Sulphate.

Fig. 5.



Cadmium and Zinc Chlorides.

Fig. 6.

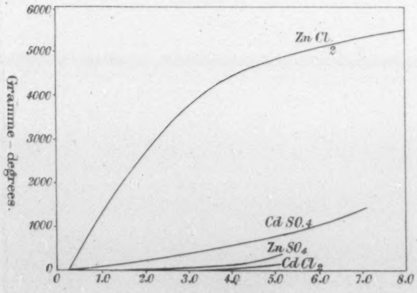
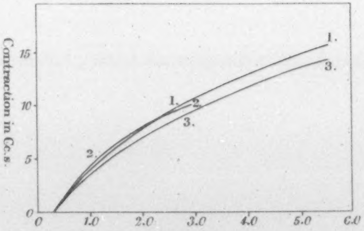


Fig. 7.



Mintern Bro's. lith.

PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

MAY 1884.

VIII. *On the Determination of Chemical Affinity in terms of Electromotive Force.*—Part VIII. *By* C. R. ALDER WRIGHT, *D.Sc.* (*Lond.*), *F.R.S.*, *Lecturer on Chemistry and Physics,* *and* C. THOMPSON, *Demonstrator of Chemistry, in St. Mary's Hospital Medical School*[*].

[Plate V.]

On the Electromotive Force set up during Interdiffusion.

147. It is well known that the E.M.F.'s of cells like those of Daniell and of Grove vary with the degree of concentration of the solutions used therein, and many measurements of the amounts of such variations have been from time to time published by different experimenters, *e. g.* by Regnault (*Ann. de Chim. et de Phys.* [3] xliv. p. 453), Svanberg (Pogg. *Annalen*, lxxiii. p. 290 [1848]); and more recently by Streintz (Carl. *Rep.* xv. p. 6 [1879]), Baumgartner (*ibid.* xv. p. 105 [1879]), and Fromme (*Annalen der Physik*, viii. p. 326 [1879]). From various causes, the nature of which will be apparent later on, the figures obtained by different observers do not exhibit such a degree of concordance as to lead to the establishment of any fundamental principle coordinating the variation in E.M.F. with the degree of dilution of the solutions used, excepting this

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[*] Read January 26, 1884.

general rule, that when the strength of the copper sulphate in a Daniell cell or of the nitric acid in a Grove's cell is decreased, a fall in the E.M.F. results; and that when the strength of the solution surrounding the zinc is decreased, a rise in E.M.F. ensues, provided the solution is one of zinc sulphate: with other salts, and with dilute sulphuric acid, some observations indicate rise, others fall, in E.M.F. with decrease of strength.

It has been shown by Moser (*Annalen der Physik*, iii. p. 216 [1878]) that when two solutions of the same metallic salt, but of unequal strengths, are allowed to communicate so as to mix by interdiffusion, a current is set up passing from the weaker to the stronger solution through the fluid when electrodes are employed of the metal contained in the salt used (*e.g.* zinc for solutions of zinc sulphate, copper for solutions of copper sulphate, and so on); whilst the experiments described in Part V. (§ 110) indicate that the variations in E.M.F. of a Daniell cell containing zinc-sulphate solution round the zinc, according as the zinc-sulphate or the copper-sulphate solution varies in strength, are approximately equal numerically to the values obtained by Moser as the E.M.F.'s set up by the interdiffusion of solutions of zinc sulphate or of copper sulphate respectively, with the same limits of strength of solution.

It seemed of interest to pursue this point further, so as to decide by accurate measurements how far this approximation is merely an accidental coincidence: accordingly a large number of experiments have been made, mostly described in the following pages.

At first the observations were made by means of the quadrant electrometer, no permanent current passing; but it was found that the experimental and observational errors were such that unless a very large number of duplicate cells were prepared and very many observations made with each, involving an immense expenditure of labour and time, trustworthy averages could not be obtained. The electrometer-readings (deflections on both sides of zero) could, at best, be read to no nearer than ±·0025 volt; so that averages for single-cell values with a probable error of not more than ±·001 volt (one millivolt) entailed a large number of readings for each cell; and as the values for different cells thus obtained exhibited a range of several millivolts, numerous duplicate cells had to be set up to obtain a final mean with a probable error of less than ±1 millivolt as the E.M.F. of each kind of cell: whilst, finally, the differences between the mean E.M.F.'s thus obtained exhibited, when plotted, deviations from a regular mean curve approaching to ±1 millivolt, even with the utmost care in making observations and the bestowal of much time in so doing. Accordingly, the method of observation was changed, a delicate galvanometer being substituted for the electrometer; the instrumental errors being smaller and the sensitiveness greater[*], the same degree of accuracy (*i. e.* the same limits of probable error) were found to be attainable with a notably smaller number of observations, provided that certain precautions were observed, detailed more fully later on (§§ 149, 150). It was soon found, however, that the observance of these precautions sufficed to permit of the method of opposition being used so as to obtain directly the difference in E.M.F. between two cells alike in all respects, save that the zinc (or copper) sulphate solution used in one was stronger than that in the other. The values thus obtained led to sensibly the same mean curves as those obtained with a far greater amount of labour by means of the electrometer, and, notwithstanding the diminution in the number of observations, the range of probable error was sensibly diminished.

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[*] The galvanometer (by Elliott) was capable of being adjusted so as to give a total deflection, reading on both sides of zero with a reversing-key, of upwards of 200 scale-divisions when the current from a Daniell cell was passed through a resistance of 100,000 ohms, using the $\frac{1}{1000}$ shunt; so that one scale-division $= \frac{1{\cdot}114}{1000 \times 100{,}000 \times 200}$ ampere $= {\cdot}000056$ micro-ampere.

It being convenient to have some term representing the millionth of a millionth (${\cdot}000000000001 = 10^{-12}$), it is proposed to use the prefix "elasso" for this purpose (from ἔλασσον), just as "micro" represents 10^{-6}, and "mega" represents 10^{6}: the value of 1 scale-division as above then becomes 56 *elasso-amperes*. The fraction ${\cdot}000000001 = 10^{-9}$ may be conveniently represented by the double prefix "milli-micro," using each half in its ordinary sense; so that a centimetre = 1 *milli-micro earth-quadrant*. In the same kind of way 1,000,000,000 ohms may be termed a *kilomegohm*; and a million of million ergs may be spoken of as a *meizerg* (μεῖζον). This nomenclature seems to be practically more convenient than such terms as twelfth-ampere, ohm-nine, erg-twelve, &c.

One of the essential precautions being the avoidance of diminution in E.M.F. in consequence of so-called "polarization," by using currents of only minute density, it at once suggested itself that under these conditions in all probability the difference of potential set up between (for example) two plates of zinc immersed in zinc-sulphate solutions of different strengths allowed to intermix by interdiffusion (or what may be conveniently called a *diffusion-cell*) would vary little, if at all, from that set up between the same two plates immersed in the same solutions respectively when these solutions are not directly connected so as to interdiffuse, but are severally connected (by any of the means used in two-fluid cells) with solutions of copper sulphate of identical strengths, in which are immersed copper plates of the same surface-character connected together by a wire : *i. e.* that subsisting between the terminal plates of two opposed Daniell cells containing the same copper-sulphate solution, but zinc solutions differing from each other in strength and respectively identical with those used in the diffusion-cell, when the copper plates are united together and the zinc plates are the terminals. On trying the experiment this was found to be the case, *sensibly identical mean curves being obtained for given variations in solution-strength and for given kinds of plate-surfaces, whether the method of opposition was used, or that of diffusion-cells.*

148. Whichever method of observation was employed, the following general laws were always verified with a high degree of exactitude whenever sufficient observations were taken to get average results with only a small probable error. All the observations were carried out in every instance at a temperature within a very few degrees of 18° C., almost invariably between 15° and 20°.

(1) In any two-fluid cell containing solutions of two metallic salts and plates of the respective metals contained therein, an *increase in strength of the solution surrounding the plate acquiring the higher potential, in virtue of the normal action of the cell* (*i.e.* the plate functioning as the copper plate of a Daniell cell), *causes an increment in the potential-difference set up between that plate and the other.* The opposite effect is always produced by an increase in the strength of the solution surrounding the other plate. The increment and decrement

thus producible are, in certain cases, very considerable: with a Daniell cell a difference of nearly 6 centivolts (or upwards of 5 per cent. of the total E.M.F.) is producible, according as strong copper-sulphate and weak zinc-sulphate solutions are taken, or *vice versâ*; with cells containing zinc and cadmium chlorides analogous differences up to even 30 centivolts are thus producible.

(2) A "law of summation" holds, expressible thus:—*The effect of the sum of a series of changes in the strengths of the solutions in a two-fluid cell is equal to the algebraic sum of the effects of each change severally.* Thus, by increasing the strength of the copper-sulphate solution in a Daniell cell (from, say, $\cdot 25\ CuSO_4\ 100\ H_2O$ * to $2\cdot 0\ CuSO_4\ 100\ H_2O$), a given increment in E.M.F. ensues, $=a$: by similarly varying the zinc-sulphate solution (from, say, $\cdot 25\ ZnSO_4\ 100\ H_2O$ to $5\cdot 0\ ZnSO_4\ 100\ H_2O$), a decrement ensues, $=b$. Then the difference in E.M.F. between two cells, one containing $\cdot 25\ CuSO_4\ 100\ H_2O$ and $\cdot 25\ ZnSO_4\ 100\ H_2O$, and the other containing $2\cdot 0\ CuSO_4\ 100\ H_2O$, and $5\cdot 0\ ZnSO_4\ 100\ H_2O$, is the sum of these amounts, *i. e.* is $a-b$; so that if e is the E.M.F. of the first and E that of the second, $E=e+a-b$.

Similarly, if three cells be compared, alike in all respects save that the copper-sulphate solutions have (for example) the strengths $\cdot 25\ CuSO_4$, $1\cdot 0\ CuSO_4$, and $2\cdot 0\ CuSO_4$ (per $100\ H_2O$ in each case), the excess of E.M.F. of the second over the first being experimentally found $=c$, and that of the third over the second being similarly found $=d$, then $a=c+d$.

(3) The values of a, b, c, d, ... *are independent, not only of the actual strength of the solution which does not vary in any two cells compared, but also of the nature of that solution and of the metal immersed in it.*

For example, in zinc-copper-sulphate cells with amalgamated zinc and electro-copper plates, the effect of a given alteration in the strength of the zinc-sulphate solution is sensibly the same whether the copper-sulphate solution be strong or weak; and, further, is precisely the same in zinc-cadmium-sulphate, or in zinc-silver-sulphate cells set up with amalgamated zinc plates. Similarly, the numerical value of the effect of a given alteration in the strength of the copper-sulphate solution is the same whether the zinc-sulphate solution be strong or weak; and, further, is still the same in copper-cadmium-sulphate or copper-silver-sulphate cells set up with electro-copper plates [*].

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* Instead of expressing molecular strengths in the form $MSO_4\ nH_2O$, and so on, it is more convenient for certain purposes to express them in the form $mMSO_4\ 100H_2O$, and so on.

(4) The values of $a, b, c, d, \ldots\ldots$ *vary perceptibly with the nature of the plate-surface of the metal immersed in the varying solution; i. e.* they are not constant for a given difference in strength if the plate-surface vary. In the case of the metals copper, zinc, and cadmium the highest values are observed, *cæteris paribus*, with plates superficially amalgamated, the amalgam being *fluid*; plates freshly electro-coated give lower values, and bright polished plates of fused metal lower values still.

(5) With the majority of kinds of plate-surface examined, the values of a and b in the expression

$$E=e+a-b$$

are such that a and b are unequal in magnitude for equal amounts of variation in the strength of the two solutions in a two-fluid cell. Sometimes a increases more rapidly than b in numerical value as the solution-strength increases; in which case the E.M.F. of the combination rises with the strength of the solutions when both are always of equal molecular strength: such a case is presented by a zinc-copper-sulphate cell with electro-zinc and amalgamated copper plates (§ 154). Sometimes the opposite is the case, *e. g.* a zinc-cadmium-chloride cell with amalgamated zinc and electro-cadmium plates (§ 156). Zinc-copper-sulphate cells set up with amalgamated zinc and electro-copper plates show the peculiarity that a and b are nearly equal numerically for all solution-strengths; so that the E.M.F. of such a Daniell cell *is practically invariable no matter what the strength of the solutions of zinc and copper sulphate used, provided that these are of the same molecular strength.*

(6) On contrasting the values of $a, b, c, d, \ldots\ldots$ with the

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[*] In copper-silver-sulphate cells the effect of a given increment in the strength of copper-sulphate solution is, of course, to *diminish* the E.M.F. of the cell, and not to increase it as in zinc-copper-sulphate cells.

E.M.F.'s corresponding to the amounts of heat developed on intermixture of gramme equivalents of the two strengths of the varying solution compared together, *the former are usually found to exceed the latter*, sometimes by a very considerable amount.

149. In carrying out observations by means of either the method of opposition or that of diffusion-cells, it is obvious that the current observed produced through a given total resistance only represents the E.M.F. due to difference of solution-strength, provided that the two zinc plates and the two copper plates are identical in surface-characters, and provided also that the current-density is small enough to reduce polarization to negligible amounts. In practice it is impossible to ensure equality of surface with any pair of plates, even though prepared with the greatest care in precisely the same way from the same mass; and the result is that when two plates, apparently identical, are immersed in the same solution, one is sufficiently electropositive with reference to the other to cause a distinctly measurable current to flow through even a large external resistance. In order to form some estimate as to the probable magnitude of this source of error, a large number of observations were made with pairs of zinc plates immersed in zinc-sulphate solutions of varying strengths, and pairs of copper plates immersed in copper-sulphate solutions. The following results in millivolts were obtained with upwards of 120 pairs of plates, readings being taken every few minutes for about half an hour after the first immersion, and being then averaged. As a rule the currents observed increased somewhat as time elapsed, so that the first readings were usually the minima. The galvanometer-readings were translated into volts by means of the formula

$$e=\frac{m}{n}\cdot\frac{R_2}{R_1}\cdot\frac{D}{1000}=mR_2\,.\,C,$$

where m = the galvanometer-reading to be translated (no shunt being used).

n = the galvanometer-reading when a Daniell cell of E.M.F. D is used to send a current through a total resistance R_1 ohms, employing $\frac{1}{1000}$ shunt.

R_2 = total resistance in circuit when the reading m is taken.

C = current representing 1 scale-division $= \frac{D}{1000nR_1}$ amperes.

If the potential differences are expressed in millivolts, then

$$e=\frac{m}{n}\cdot\frac{R_2}{R_1}\cdot D.$$

Bright Zinc Plates.			
Molecular strength of solution, per 100 H_2O.	Near 5 MSO_4.	MSO_4 to 2 MSO_4.	·25 MSO_4 to ·5 MSO_4.
Maximum	1·49	3·65	12·5
Minimum	·07	·32	·32
Average	·69	2·13	5·45
Amalgamated Zinc Plates.			
Maximum	·11	·15	1·55
Minimum	·01	·02	·01
Average	·07	·09	·69
Bright Copper Plates.			
Maximum	......	3·15	2·6
Minimum	......	·65	·48
Average	......	1·95	1·53
Recently coated Electro-copper Plates.			
Maximum	......	·66	·22
Minimum	......	·03	·03
Average	......	·21	·14
Amalgamated Copper Plates.			
Maximum	......	·54	1·4
Minimum	......	·08	·27
Average	......	·28	1·0

As a general rule the weaker the solution the greater is the average difference of potential set up between two plates, as alike as practicable, immersed in the same fluid : *cæteris paribus*, bright plates show much wider limits of variation than amalgamated or electro plates.

It being impossible to ensure equality of surface-conditions by simply taking pains to make plates as alike as practicable, an approximation to the value that would have been obtained, had the plates been equal in surface-conditions, was arrived at in each experiment by the simple device of exchanging the plates after one series of readings had been taken, and taking another series of readings, averaging the two mean values thus obtained. In many cases the plates were exchanged twice more, and the general mean of all four sets of readings taken. To prevent alteration of solution-strength, the plates exchanged were always rinsed with the solution into which they were about to be dipped before immersion therein. Operating in this way, the difference between the values obtained before and after exchanging represents *double* the sum of the potential difference that would be set up between the plates when opposed to one another in the same solutions respectively. It is noteworthy that the figures thus got by exchanging plates are of the same order of magnitude as those resulting from the opposition of two plates of the same kind. Thus in the above-described experiments the maximum variation observed with amalgamated zinc plates is 1·55 millivolt, and that with electro-copper plates ·66 millivolt, giving a sum of 2·21; whilst the corresponding average values give a sum of less than ·5 millivolt. With two opposed Daniells set up with amalgamated zinc and electro-copper plates, the halves of the differences observed on exchanging plates averaged less than ·5 millivolt, sometimes, however, amounting to 1·0, and occasionally, but only rarely, to 2·0 millivolts; and similarly in other cases.

150. In order to eliminate errors arising from depreciation of E.M.F. through non-adjuvancy, arising from the current-density being greater than the limiting-density below which such effects are inappreciable (" polarization "), several series of observations were made in order to find out what the limiting-densities are for different kinds of plates and fluids, such that the depreciation in E.M.F. shall not exceed a definite small quantity, say ·1 to ·2 millivolt. The experiments already published made with single Daniell and other analogous cells (§§ 103–105, Part V.) show that with current-densities of from 10 to 20 microamperes per square centimetre of plate-surface (both plates being equal in area, and

one only being reckoned), diminutions in E.M.F. of from 1 to 6 millivolts may be brought about, quantities in many cases far exceeding the potential-differences due to varying solution-strength to be measured. Manifestly, therefore, only very minute currents can be employed when two Daniell or other analogous cells are opposed, and consequently the effect of "polarization" about doubled. Similarly the experiments described in Part IV. (§ 93) indicate that when a current passes between two zinc plates in zinc-sulphate solution, or between two copper plates in copper-sulphate solution, a "counter electromotive force" of a considerable number of millivolts, and even some centivolts, may be set up with current-densities of but a few microamperes per square centimetre; so that in a "diffusion-cell" serious diminutions in the potential-difference actually set up may be brought about by very small current-densities.

In order to determine these limiting current-densities, experiments were made in the following way. The diffusion-cell, or pair of opposed Daniell or other cells to be examined, was set up, as was also a normal Daniell cell for comparison, and the currents from each alternately sent through a large external resistance (using appropriate shunts), series of readings being taken in each case. The resistance was now altered, and two fresh series of readings taken; after which it was again altered, and two more series taken, and so on: usually the whole set of series of readings was repeated in reverse order. The average scale-readings for a series of given total resistances in circuit were thus known both for the Daniell cell and the other one compared with it. With the former, the product of average scale-reading and total resistance was sensibly constant for current-densities that caused an appreciable falling-off in the product similarly obtained with diffusion-cells or with two opposed Daniell cells, &c., showing that whilst "polarization" did not occur to a measurable extent in the first case, it did in the second. The following illustration will make the point clear: two series of readings with varying resistances were made in reverse order with a normal Daniell cell, and with two opposed cells jointly giving an effective E.M.F. of a little more than one-hundredth of that of the Daniell cell; for the former the $\frac{1}{1000}$ shunt was used, and for the latter the $\frac{1}{10}$ shunt.

Single Daniell Cell.

Total resistance in circuit, in ohms.	Scale-readings.			Product of mean scale-reading into resistance.
	First series.	Reversed series.	Mean.	
200,050	63·7	63·9	63·8	$12·763 \times 10^6$
150,050	84·8	85·3	85·05	$12·762 \times 10^6$
100,050	127·5	127·6	127·55	$12·761 \times 10^6$

Here the product of scale-reading into resistance being constant within the limits of observational error, it is evident that the E.M.F. of the cell was constant within about $\frac{1}{2000}$ part of its value, notwithstanding that the current rose from $\frac{1·11}{200050}$ ampere (5·5 microamperes) to $\frac{1·11}{100050}$ ampere (11·1 microamperes), representing a rise in density of from 2 to 4 microamperes per square centimetre, the plates exposing a surface of about 3 square centimetres each. Each scale-division here represented $\frac{1·115}{1000 \times 12·762 \times 10^6}$ ampere, or 87·37 elassoamperes.

Two opposed Cells.

Total resistance, in ohms.	Scale-readings.			Current, in microamperes.	E.M.F. in millivolts.	Fall in E.M.F.
	First series.	Reversed series.	Mean.			
200,820	69·3	70·1	69·7	·060897	12·23	—
150,820	92·1	93·25	92·67	·080965	12·21	·02
100,820	137·0	138·0	137·5	·120134	12·11	·11

Hence with an increase of current from ·06 to ·08 microampere, representing an increase in density from ·02 to ·027, the fall in E.M.F. was barely measurable, being only ·02 millivolt; but when the current rose to ·12 microampere, giving a density of ·04, the fall in E.M.F. was distinct, being upwards of ·1 millivolt.

151. In the same kind of way various other observations were made, and indicated on the whole that the effect of polarization in cells set up with amalgamated-zinc and electro-

copper plates is not greater than about ·2 millivolt, as long as the current-density does not exceed about ·05 microampere per square centimetre of plate-surface.

Limiting values not far from this were similarly obtained with other kinds of zinc- and copper-plate surfaces. Accordingly in the observations made with these kinds of cells for the purpose of estimating the variations in E.M.F. due to difference in solution-strength, the current-densities were never allowed to exceed this limit, and were usually a long way below it.

In precisely the same kind of way the limiting values for various kinds of diffusion-cells were arrived at. The following table represents some of the average results obtained, the E.M.F.'s being expressed in millivolts:—

Current-density, microamperes per square centimetre.	Two opposed Daniell cells.	Diffusion-cells.		
		Zinc sulphate.		Copper sulphate.
	Amalgamated zinc and electro-copper plates.	Electro-zinc plates.	Amalgamated-zinc plates.	Electro-copper plates.
Not exceeding ·02	Below 0·02	Below ·03	Inappreciable	Inappreciable
·02 to ·035	„ 0·1	„ ·1	Below ·1	Below ·1
·035 „ ·06	·1 to ·3	·1 to ·2		
·06 „ ·10	·3 „ ·5	·2 „ ·5		0·1 to ·3
·10 „ ·15	·5 „ ·8	·5 „ 1·0	·1 to ·2	·3 „ ·5
·15 „ ·2	·8 „ 1·2		·2 „ ·4	·5 „ ·8
·2 „ ·5			·4 „ 1·0	·8 „ 2·0
·5 „ ·8			1·0 „ 2·0	

It is here noticeable that the amounts of depreciation for given increments in current-density observed with two opposed Daniell cells containing amalgamated-zinc and electro-copper plates are fairly close to the sums of those similarly observed for two diffusion-cells, one containing amalgamated-zinc and the other electro-copper plates. The chemical action in two opposed Daniell cells amounts to solution of copper in one cell and deposition thereof in the other, and ditto for zinc; or precisely the sum of the actions with two diffusion-cells.

The amount of depreciation for a given current-density increase varies notably with the metal and character of surface: thus amalgamated zinc gives less depreciation than electro-copper, and electro-copper less than electro-zinc. Variation in the strength of the solution used did not appear to influence the result to anything like so great an extent as variation in the nature of the plate-surfaces.

On the whole it was found, even in those cases where the maximum amount of depreciation was produced, that this depreciation did not exceed from ·1 to ·2 millivolt, until the current-density overpassed ·02 to ·03 microampere per square centimetre. In the four cases above cited the limiting current-densities, when the depreciation amounts to ·2 millivolt, are:—

Two opposed Daniell cells, amalgamated-zinc and electro-copper plates	·05
Diffusion-cells, electro-zinc plates	·06
„ „ amalgamated-zinc plates	·15
„ „ electro-copper plates	·08

In carrying out the observations, therefore, care was taken* that in no case should the current-density exceed the limiting value for the particular class of cell examined, current-densities of much less amount being in most cases employed; so that, finally, *the effect of "polarization" on the average values obtained is in no case to depreciate them by a quantity so great as ·2 millivolt, and is usually insufficient to depreciate by an amount approaching to ·1 millivolt.*

152. As a general rule, it was found that when the cell (or pair of opposed cells) to be examined was set up, comparatively little variation in the current flowing took place during 15 to 30 minutes; what alteration did occur being evidently due to alteration in condition of plate-surface (by superficial oxidation by dissolved air, or by molecular change, *i.e.* spontaneous change of state of aggregation, or by solution or deposition of external film as the current flowed producing electrolysis), and being only a fraction of the variation produced on exchanging plates. With bright zinc plates, however, the alteration during a few minutes after setting up was

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[*] Owing probably to the influence of "polarization," the values obtained by Fromme, *loc. cit. suprà*, do not exhibit very close concordance with one another, nor do the mean curves thence deducible agree sharply with those subsequently detailed. Moser's diffusion-cell figures, on the other hand, do not differ widely from those obtained by us.

often considerable and irregular in direction. The numbers given in the subsequent section are in all cases deduced from the average readings of the cells during the first 15 or 20 minutes after first setting up, or after exchanging plates, as the case might be; the mean of the two averages thus obtained (or of the four, if three exchanges were made after taking the first set of readings) being finally adopted as the mean value for the particular experiment.

As regards the experiments with the diffusion-cells, these were ordinarily constructed of two beakers united by an inverted Y-shaped tube, the ends of which were covered with bladder or other thin membrane, and filled with either of the two solutions used, one in one beaker, the other in the other: in short, they were precisely similar to the forms of Raoult cell used in the preceding portions of these researches. It was thought desirable to see if any influence could be traced as exerted by the membranes as such, and accordingly a number of gravity diffusion-cells were set up by pouring into a long U-tube the stronger of the two solutions used until rather more than half full, and then very cautiously running slowly into one limb the weaker solution, so as to have a well-marked line of demarcation between the two fluids. Two plates were then immersed in the two solutions and exchanged after taking readings, and so on. Both with zinc sulphate and copper sulphate no measurable differences could be detected between the average results obtained with these cells and with the Raoult form of cell, both sets of cells having respectively the same fluids and kinds of plates; clearly proving that the membranes as such exercised no measurable influence on the results.

As an illustration of the general character of the experiments made, the following observations with two opposed Daniell cells may be cited as an example, typical in all respects saving, first, that the values obtained before and after exchanging plates differ more than usual (for which reason this experiment is selected); and, secondly, that the galvanometer was regulated so as to be considerably less sensitive than was found desirable for other experiments, on account of the comparatively large potential-difference to be measured.

Plates used: amalgamated zinc and electro-copper.

Solutions used: per 100 H_2O, 2·0 $CuSO_4$ throughout; 5·584 $ZnSO_4$ in one cell and ·1012 $ZnSO_4$ in the other.

Valuation of scale: a normal Daniell cell (set up with amalgamated zinc, electro-copper, and zinc- and copper-sulphate solutions of equal strength) gave 125·7 scale-degrees as mean reading when 200100 ohms were in circuit, the $\frac{1}{100}$ shunt being used, whence 1 scale-division $= \frac{1\cdot114}{100 \times 200100 \times 125\cdot7}$ ampere = ·000443 microampere = 443 elassoamperes.

	Readings before exchanging plates.	After exchanging plates.
Average scale-reading (no shunt used)	484·25	467·0
Currrent passing, in microamperes*	·2145	·2069
Total resistance in circuit, in ohms	207400	207400
E.M.F., in millivolts	44·5	42·9

Mean of the two results .... 43·7 millivolts.
Maximum departure between ditto . 1·6 millivolt.
Difference from mean .... ±·8 „

In the same kind of way other similar experiments gave means ranging from 41·6 to 44·4 millivolts, the final average being 43·3, with a probable error of ±·34 millivolt.

153. The following tables give, in millivolts, the results obtained with various kinds of metals, natures of plate-surfaces, and descriptions of saline solutions :—

I. *Variations of Potential due to Variations of Strength in Zinc-sulphate Solution.*

1. *Amalgamated Zinc Plates.*

A. Observations with the Electrometer.

Probable error of each value cited not exceeding ±1·0 millivolt. The numbers represent the difference of potential set up when one solution is m $ZnSO_4$ 100 H_2O, and the other n $ZnSO_4$ 100 H_2O.

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[*] Representing a current-density of about ·045 microampere per square centimetre.

Value of *m*.	Value of *n*.					
	4·2	3·0	2·1	1·1	·55	·167
5·1	4	12	16	23	28	37
4·2	……	8	12	19	24	33
3·0	……	……	4	11	16	25
2·1	……	……	……	7	12	21
1·1	……	……	……	……	5	14
·55	……	……	……	……	……	9

B. With two opposed Daniell cells, the copper plates being united and the zinc plates the terminal ones, the following values were obtained. The probable error of each value cited is less than in the electrometer-experiments, being usually well within ±·5 millivolt, often no more than ±·25 millivolt.

Value of *m*.	Value of *n*.					
	3·995	3·005	2·158	1·016	·497	·1012
5·584	10·5	16·1	20·2	26·7	32·3	43·3
3·995	……	5·6	9·7	16·2	21·8	32·8
3·005	……	……	4·1	10·6	16·2	27·2
2·158	……	……	……	6·5	12·1	23·1
1·016	……	……	……	……	5·6	16·6
·497	……	……	……	……	……	11·0

C. With Diffusion-cells the following values were obtained: probable error of each value less than ±·5 millivolt:—

Value of *m*.	Value of *n*.					
	3·95	3·10	2·00	·96	·50	·237
5·25	6·8	12·4	18·4	24·7	29·2	35·0
3·95	……	5·6	11·6	17·9	22·4	28·2
3·10	……	……	6·0	12·3	16·8	22·6
2·00	……	……	……	6·3	10·8	16·6
·96	……	……	……	……	4·5	10·3
·50	……	……	……	……	……	5·8

On graphical representation all three sets of figures are found to accord fairly well when, by interpolation, the figures are all reduced to a common origin for the three curves, viz. when $m=5·0$. The following table gives the result thus reduced to common origin and the same abscissæ.

	Electrometer.	Two opposed cells.	Diffusion-cells.	Average.
5·584	……	− 3·8		
5·25	……	……	− 1·3	
5·1	− 0·4	……	……	
5·0	0	0	0	0
4·0	4·8	6·7	5·2	5·6
3·0	11·6	12·3	11·6	11·8
2·0	16·3	17·3	17·1	16·9
1·0	23·5	23·1	23·1	23·2
·5	28·7	28·5	27·9	28·4
·237	34·9	35·7	33·7	34·8
·167	36·6	37·7	……	37·2
·100	……	39·5	……	39·5

It is evident that, having regard to the impossibility of completely eliminating errors from difference of character of plate-surface, these numbers coincide sufficiently closely to show that whether no current at all circulates (electrometer), or a small current not too great to set up any notable "polarization," *sensibly the same numbers result whether the observations be made by carefully valuing separate cells and subtracting the values from one another; by opposing two cells and measuring the current due to the difference in their E.M.F.'s; or by means of diffusion-cells* (representing the terminal liquids of two opposed cells of Raoult's form, when directly connected). The same conclusions also follow from the observations detailed in § 154 made with copper-sulphate solution and electro-copper plates.

2. *Electro-zinc Plates.*

Observations made with Diffusion-cells only: probable error in no case exceeding ± ·75 millivolt.

	$n=3{\cdot}005$	$n=1{\cdot}016$	$n={\cdot}1012$
$m=5{\cdot}584$	11·2	20·0	30·5
3·005	……	8·8	19·3
1·016	……	……	10·5

3. *Bright Zinc Plates.*

Observations with Diffusion-cells only: very much less concordance between the results of these experiments than with other kinds of zinc plates, and much more alteration (and of more irregular character) on allowing cells to stand a few minutes.

Probable error about ± 1·5 millivolt.

	$n=3{\cdot}005$	$n={\cdot}1012$
$m=5{\cdot}584$	10·0	29·6
$=3{\cdot}005$	......	19·6

The following table represents these three sets of values reduced by interpolation to a common origin ($m=5{\cdot}0$) and common abscissæ: the curves respectively marked 1, 2, and 3 in fig. 1, Plate V., indicate the three sets of reduced values thus obtained.

Difference of Potential set up between Solutions of $5{\cdot}0\ ZnSO_4\ 100\ H_2O$ and $n\,ZnSO_4\ 100\ H_2O$.

	Amalgamated zinc (average above cited).	Electro-zinc.	Bright zinc.
$n=5{\cdot}0$	0	0	0
$=3{\cdot}0$	11·8	8·6	7·7
$=1{\cdot}0$	23·2	17·5	15·8
$=0{\cdot}1$	39·5	27·9	25·3

Evidently the values with amalgamated zinc are the highest, and those with bright zinc the lowest.

154. II. *Variations of Potential due to Variation in Strength of Copper-sulphate Solution.*

1. *Electro-copper Plates.*

A. Observations with the Electrometer. Probable error not exceeding ±1 millivolt.

Values of m.	Values of n.		
	1·10	·55	·167
2·1	5	11	20·5
1·1	......	6	13·5
·55	......	......	9·5

B. With two Opposed Cells. Probable error usually well within ±·5 millivolt, and often less than ±·25 millivolt.

	$n={\cdot}940$	$n={\cdot}461$	$n={\cdot}094$
$m=1{\cdot}972$	5·6	10·3	22·4
$={\cdot}940$	......	4·7	16·8
$={\cdot}461$	......	......	12·1

C. With Diffusion-cells. Probable error less than ±·5 millivolt.

	$n = \cdot 99$	$n = \cdot 47$	$n = \cdot 227$
$m = 1{\cdot}88$	5·7	10·5	16·3
$= \cdot 99$	......	4·8	10·6
$= \cdot 47$	......	......	4·7

On graphical representation after reduction, by interpolation, to common origin (when $m = 2{\cdot}0$) and common abscissæ, these three sets of figures are found to coincide within reasonable error-limits, thus confirming the results arrived at above with amalgamated-zinc plates and zinc-sulphate solutions. Further, it is noticeable that these values are all close to those similarly obtained with zinc-sulphate solutions and amalgamated-zinc plates when similarly reduced.

Value of m.	Electrometer.	Two opposed cells.	Diffusion-cells.	Average.	Average with zinc sulphate and amalgamated-zinc plates.
2·1	−·5	......			
2·0	0	0	0	0	0
1·972	......	·2	......	......	......
1·88	......	......	·8	......	......
1·0	5·6	5·5	6·4	5·8	6·3
·5	11·7	10·1	11·0	10·9	11·5
·227	18·5	18·2	17·1	17·9	18·2
·167	20·0	20·2	......	20·1	20·3
·100	21·7	22·4	......	22·0	22·6
·094	21·8	22·6	......	......	......

It would hence result that the E.M.F. of a Daniell cell set up with zinc- and copper-sulphate solutions *of the same molecular strength*, and amalgamated-zinc and electro-copper plates, cannot exhibit any very marked variation, whatever the actual strength of the solutions, inasmuch as whatever effect on the E.M.F. is produced by a given variation in the strength of the zinc-sulphate solution must be very nearly counterbalanced by the equal and opposite effect of the same variation in the strength of the copper-sulphate solution. If, however, electro-zinc or bright zinc plates be used, the E.M.F. must rise with the strength of the solutions, the copper-sulphate variation effect overpowering the zinc-sulphate variation effect. In other words, if *e* be the E.M.F. of the cell for a given low strength of solution, and E that for a greater strength, then $E=e+a-b$ (§ 148): with amalgamated zinc and electro-copper plates, a nearly $=b$; but with electro or bright zinc, $a<b$.

The following experiments show that the value of a, *cæteris paribus*, is greater with amalgamated, but less with bright, than with electro copper; so that with cells set up with amalgamated zinc plates, the value of the E.M.F. rises with the strength of the solutions when amalgamated copper plates are opposed, and falls when bright copper plates are used instead.

2. *Amalgamated Copper Plates.*

Observations with Diffusion-cells. Probable error not exceeding ± ·75 millivolt.

	$n=·940$	$n=·461$	$n=·094$
$m=1·972$	6·0	12·0	27·5
·940	......	6·0	21·5
·461	......	......	15·5

3. *Bright Copper Plates partially but not completely Electro-coated.*

Observations with Diffusion-cells. Probable error not exceeding ± ·75 millivolt.

	$n=·940$	$n=·461$	$n=·094$
$m=1·972$	4·1	9·3	19·7
·940	......	5·2	15·6
·461	......	.. . .	10·4

4. *Bright Copper Plates.*

Observations with Diffusion-cells. Probable error not exceeding ±1·0 millivolt.

	$n=·461$	$n=·094$
$m=1·972$	6·9	16·8
·461	......	9·9

The following table represents these four sets of values reduced, by interpolation, to a common origin ($m=2·0$) and common abscissæ: the curves marked respectively 1, 2, 3, and 4, fig. 2, represent these sets of reduced values: curve 5 similarly represents the average values for amalgamated zinc and zinc-sulphate solution similarly reduced; evidently nearly coinciding with curve 2 (electro-copper).

Difference of Potential set up between Solutions of 2·0 $CuSO_4$ 100 H_2O and $n$$CuSO_4$ 100H_2O.

	Amalgamated copper.	Electro-copper.	Bright copper only partially electro-coated.	Bright copper.
n=2·0	0	0	0	0
=1·0	5·9	5·8	4·0	3·5
= ·5	11·7	10·9	9·0	6·6
= ·1	27·2	22·0	19·6	16·8

155. A number of observations were similarly made with various cadmium-sulphate solutions, employing different kinds of cadmium plates: only diffusion-cells were used in this series of experiments. The following results were obtained as final average values, showing that amalgamated plates (wet with liquid amalgam) give higher, and bright plates lower values than electro-coated plates, just as with zinc and copper.

1. *Electro-cadmium Plates.*—Probable error of each value less than ± ·5 millivolt.

Value of m.	Value of n.					
	4·95	3·205	2·01	1·02	·46	·235
6·10	6·0	14·2	19·5	24·7	29·9	34·2
4·95	......	8·2	13·5	18·7	23·9	28·2
3·205	......	......	5·3	10·5	15·7	20·0
2·01	......	......	......	5·2	10·4	14·7
1·02	......	......	......	......	5·2	9·5
·46	......	......	......	......	......	4·3

2. *Bright Cadmium Plates.*—Probable error less than ± ·75 millivolt.

Value of m.	Value of n.					
	4·95	3·205	2·01	1·02	·46.	·235.
6·10	4·9	13·7	18·5	23·0	27·4	30·5
4·95	......	8·8	13·6	18·1	22·5	25·6
3·205	......	......	4·8	9·3	13·7	16·8
2·01	......	......	......	4·5	8·9	12·0
1·02	......	......	......	......	4·4	7·5
·46	......	......	......	......	......	3·1

3. *Amalgamated Cadmium.*—Surface wet with fluid amalgam. Probable error not exceeding ±·75 millivolt.

	$n=2{\cdot}01$.	$n=1{\cdot}02$.	$n={\cdot}235$.
$m=6{\cdot}10$......	20·6	26·3	35·9
$=2{\cdot}01$.....	......	5·7	15·3
$=1{\cdot}02$......	......	......	9·6

4. *Amalgamated Cadmium.*—Surface not fluid, but crystalline. Probable error not exceeding ± 1·5 millivolt.

	$n=2{\cdot}01$.	$n=1{\cdot}02$.	$n={\cdot}235$.
$m=6{\cdot}10$	14·5	19·6	24·5
$=2{\cdot}01$	......	5·1	10·0
$=1{\cdot}02$	......	......	4·9

The following tables are obtained from the above values by interpolation, as in the above observations with zinc and copper sulphates:—

Difference of Potential set up between Solutions of $5{\cdot}0\,CdSO_4\,100\,H_2O$ and $n\,CdSO_4\,100\,H_2O$.

	Amalgamated cadmium, fluid.	Electro-cadmium.	Bright cadmium.	Amalgamated cadmium, crystalline.
$n=5{\cdot}0$........	0	0	0	0
3·0........	10·1	9·9	10·5	7·1
2·0........	15·1	13·9	13·8	10·6
1·0........	20·9	19·2	18·4	15·8
0·5........	25·6	23·8	22·4	18·3
0·235......	30·4	28·5	25·8	20·6

Difference of Potential set up between Solutions of $2{\cdot}0\,CdSO_4\,100\,H_2O$ and $n\,CdSO_4\,100\,H_2O$.

	Amalgamated cadmium, fluid.	Electro-cadmium.	Bright cadmium.	Amalgamated cadmium, crystalline.
$n=2{\cdot}0$.........	0	0	0	0
$=1{\cdot}0$.........	5·8	5·3	4·6	5·2
$={\cdot}5$.........	10·5	9·9	8·6	7·7
$={\cdot}235$......	15·3	14·6	12·0	10·6

Curves 1 to 4 (figs. 3 and 4) represent these sets of values respectively: it is noticeable that the curve obtained with crystalline amalgam plate-surfaces underlies the others.

On contrasting the first of these tables with that similarly obtained with zinc sulphate (§ 153), and the second with that obtained with copper sulphate (§ 154), it is evident that with certain kinds of plates the effect of an increase in strength of solutions (both being always of equal strength) is to produce an increase in E.M.F. in zinc-cadmium-sulphate cells or cadmium-copper-sulphate cells; and with other kinds of plates to produce a decrease: *i. e.* the values of a and b in the formula

$$E=e+a-b$$

are such that in certain cases $a>b$ and in others $b>a$, precisely as is found with zinc-copper-sulphate cells. It is noticeable that even in the most extreme cases the difference between a and b is never very great, rarely exceeding a few millivolts.

156. For the sake of comparison with the amounts of heat developed on intermixture of strong and weak solutions, the following series of observations were made with solutions of zinc and cadmium chlorides, these salts being more especially selected because the calorimetric observations detailed later on (§ 160) showed that, whereas the heat of dilution of cadmium-sulphate solutions is greater than that of zinc-sulphate solutions, the opposite relationship holds with the solutions of the chlorides of these metals.

Cadmium Chloride.—Observations with diffusion-cells. Electro-cadmium plates: probable error of each value not exceeding ±·5 millivolt.

Value of *m*.	Value of *n*.					
	8·0.	4·45.	3·1.	2·1.	·67.	·25.
11·1	16·1	23·8	26·4	33·1	43·3	54·4
8·0	......	7·7	10·3	17·0	27·2	38·3
4·45	......	......	2·6	9·3	19·5	30·6
3·1	......	......	......	6·7	16·9	28·0
2·1	......	......	......	......	10·2	21·3
·67	......	......	......	......	......	11·1

Zinc Chloride.—Observations with diffusion-cells. Amalgamated-zinc plates: probable error less than ±1·0 millivolt.

Value of *m*.	Value of *n*.						
	9·8.	6·1.	3·3.	2·04.	·754.	·25.	·172.
24·4	112·0	186·3	207·1	218·1	239·7	254·1	259·0
9·8	......	74·3	95·1	106·1	127·7	142·1	147·0
6·1	......	......	20·8	31·8	53·4	67·8	72·7
3·3	......	......	......	11·0	32·6	47·0	51·9
2·04	......	......	......	......	21·6	36·0	40·9
·754	......	......	......	......	......	14·4	19·3
·25	......	......	......	......	......	......	4·9

On reducing these two sets of figures to the values for $m=10$ as origin, and plotting the resulting numbers, the curves marked 1 and 2 respectively (Pl.V. fig. 5) are obtained: evidently the value of b in the expression $E=e+a-b$ greatly exceeds that of a for all cases where equal molecular strengths of solutions are used in zinc-cadmium-chloride cells; *i. e.* the E.M.F. of a cell set up with zinc and cadmium chlorides, amalgamated zinc, and electro-cadmium decreases as the solution-strength increases, both solutions being equal in strength

A number of observations made with the galvanometer showed that this is the case, and that the value of the E.M.F. of any zinc-cadmium-chloride cell is given in volts by the equation

$$E=\cdot 330+a-b,$$

where ·330 is the E.M.F. of a cell containing amalgamated-zinc and electro-cadmium plates, and solutions of the chlorides of equal strength $\cdot 25\,MCl_2\ 100\,H_2O$; whilst a and b are the values deduced from the above tables for the difference of potential set up for solutions of this strength as compared with the particular strengths employed in the cell examined.

157. A noteworthy point in connexion with the value ·330 volt for solutions $\cdot 25\,MCl_2\ 100\,H_2O$ is the following. According to Julius Thomsen (*Journ. Prakt. Chemie,* xi. p. 402), the heats of formation of cadmium and zinc sulphates dissolved in $400\,H_2O$ ($\cdot 25\,MSO_4\ 100\,H_2O$) exhibit exactly the same difference as exists between those of cadmium and zinc chlorides dissolved in $200\,H_2O$; thus:—

$Zn, O, SO_3, aq=$	106090	$Zn, Cl_2, aq=$	112840
Cd, O, SO_3, aq	89500	Cd, Cl_2, aq	96250
	16590		16590

Consequently, as the heat of dilution of $ZnCl_2\ 200\,H_2O$ to $ZnCl_2\ 400\,H_2O$ exceeds that of $CdCl_2\ 200H_2O$ to $CdCl_2\ 400\,H_2O$, and the excess is to be added to the above difference in the case of the chlorides, the heat evolved in the displacement of cadmium by zinc from $CdCl_2\ 400\,H_2O$ is slightly *greater* than that from $CdSO_4\ 400\,H_2O$. The electromotive forces of zinc-cadmium-sulphate and zinc-cadmium-chloride cells for solutions of strengths $MSO_4\ 400\,H_2O$, and $MCl_2\ 400\,H_2O$ ($\cdot 25\,MSO_4$ and $\cdot 25\,MCl_2$ per $100\,H_2O$) do not exhibit this relationship: on the contrary, the E.M.F. of the latter is materially *less* than that of the former; and, further, is distinctly less than that corresponding to the heat evolved in the net chemical change with which the E.M.F. of the former fairly coincides; thus:—

E.M.F. corresponding to 16590 gramme-degrees per gramme-molecule, or 8295 per gramme equivalent .... = ·365 volt.

Observed E.M.F. with zinc-cadmium-sulphate cells set up with solutions of ·25 MSO_4 100 H_2O, amalgamated-zinc and electro-cadmium plates (§ 121, Part VI.) .... = ·360 volt.

Observed E.M.F. with zinc-cadmium-chloride cells set up with solutions of ·25 MCl_2 100 H_2O, amalgamated-zinc and electro-cadmium plates............... = ·330 „

The difference betwen ·365 and ·330 volt, or ·035 volt, represents nearly 10 per cent. of the former value, and corresponds to upwards of 1500 gramme-degrees per gramme-molecule, a quantity almost too large to be likely to be due solely to accumulation of experimental errors. This point will be further discussed in a future paper.

158. No material difference is made in the relationships between the E.M.F.'s observed (deduced from the assumption that the E.M.F. of Clark's cell =1·457 volt) and those calculated from the heat-values (by using the factor 4410), when, instead of the numerical values 1·457 and 4410 for these quantities (hitherto purposely employed throughout for the sake of uniformity), the more exact values are used deduced from more recent observations on the true value of the B.A. unit of resistance, and especially those of Lord Rayleigh, which indicate that the true value is only $\cdot 9868 \times 10^9$. For the use of this corrected value reconciles the apparent discrepancy between Joule's various valuations of the mechanical equivalent of heat (§§ 33, 34, Part I.); and, further, causes all the different estimations of the value of J discussed in §§ 55 and 56 (Part III.) to agree fairly well together, and to become on reduction values close to the mean result of Joule's friction

experiments, viz. 41·555 megalergs (§ 34). Combining this value of J with the mean value of the "Faraday coefficient" (the quantity referred to in § 7, Part I., as indicated by χ, but which may be gracefully indicated instead by F in commemoration of Faraday) deducible from the experiments of Kohlrausch and the more recent ones of Mascart, viz. ·0001048 (§ 103, footnote, Part V.), the end result is attained that

$$JF = 41{\cdot}555 \times 10^6 \times {\cdot}0001048 = 4355.$$

Now $4355 = 4410 \times {\cdot}9875$; so that whilst the actual measurements of E.M.F. are reduced in the ratio ·9868, those deduced from heat-valuations must concurrently be reduced in the ratio ·9875, or almost exactly to the same extent. If J be taken $= 41{\cdot}5 \times 10^6$, the reduction ratio becomes ·9862 instead of ·9875. Hence it appears that in order to reduce to the values most consistent with the bulk of evidence at present extant the various E.M.F. determinations described in the previous portions of these researches, it will practically suffice to multiply them by ·987, *i. e.* to subtract 1·3 per cent. of their value, whether the figures be direct determinations of E.M.F. or deductions from calorimetric experiments.

It may further be noticed that when the value $\cdot987 \times 10^9$ for the B.A. unit is taken, in consequence that of Clark's cell becomes $\cdot987 \times 1{\cdot}457 = 1{\cdot}438$ volt; so that the mean value of the E.M.F. corresponding to the work done in electrolysing water, as directly determined in Part II. § 46, becomes $1{\cdot}4308 \times 10^8$ C.G.S. units, taking $J = 41{\cdot}555 \times 10^6$ instead of 42×10^6, as in Part II. The mean heat-valuation arrived at § 31, Part I., from the results of various experimenters employing the calorimeter, being 34100 gramme-degrees, the product $34100 \times JF$ becomes $34100 \times 4355 = 1{\cdot}4850$, which value exceeds 1·4808 by only ·29 per cent., a quantity falling within the limits of probable error in the experiments ($\pm\cdot32$ per cent.). Inasmuch as from various causes a slight systematic error of defect necessarily attended the direct determinations, the final conclusion is warranted that these direct determinations are sensibly in accordance with the two propositions, firstly that the B.A. unit is actually only $\cdot987 \times 10^8$; and, secondly, that Clark's cell has an E.M.F. of $\cdot987 \times 1{\cdot}457 = 1{\cdot}438$ volt.

159. The experiments described in §§ 153 and 154 lead to the conclusion that a Daniell cell containing solutions of zinc and copper sulphate of equal strengths has an almost invariable E.M.F. whatever the strengths of the solutions when the plates are of amalgamated zinc and electro-copper; but rises in E.M.F. if the plates are either amalgamated zinc and amalgamated copper, electro-zinc and electro-copper, or, *à fortiori*, electro-zinc and amalgamated copper. It seemed desirable to substantiate these deductions more rigorously. Accordingly two pairs of solutions of zinc and copper sulphate were carefully prepared, such that one pair had the composition $2{\cdot}069\,MSO_4\,100H_2O$, and the other the composition $\cdot0937\,MSO_4\,100H_2O$. Cells were then set up with these fluids, opposed to one another, and series of readings taken. It was found that the numbers thus obtained exhibited much greater divergences and fluctuations than those similarly obtained with cells where the molecular strengths of the solutions were not equal in each case respectively. In the latter case the current always passed in one direction, and did not exhibit any very marked alteration in magnitude during the first 15 to 30 minutes after setting up (during which period the observations above described were ordinarily made); but with two opposed Daniell cells, containing pairs of solutions of the same strengths in each severally, the differential current sometimes passed in one direction on first setting up, sometimes in the opposite direction; sometimes it increased in intensity as time elapsed, and sometimes it diminished: in the latter case occasionally it diminished to *nil*, and then flowed in the opposite direction with gradually increasing intensity. Thus, for instance, the following numbers were obtained in one set of observations where the density never exceeded ·02 microamperes per square centimetre, and was usually much less, so that "polarization" errors were eliminated (§ 150). The total resistance in circuit (including galvanometer and cells) was 107,400 B.A. units. The sign + indicates that the E.M.F. of the cell containing the stronger solutions was higher than that of the other; the sign − indicates the opposite. Readings were taken every minute for 15 minutes after setting up; the plates were then exchanged (after rinsing with the appropriate solutions), and another similar series of readings taken: a

second, and then a third exchange was similarly made, readings for 15 minutes being again taken in each case: the readings are translated into millivolts, every scale-division being equal, in these experiments, to 85·7 classoamperes, and consequently representing $85{\cdot}7 \times 10^{-12} + 107{,}400 = {\cdot}00000895$ volt = 8·95 microvolts.

Minutes after first setting up.	Before plates exchanged.	After first exchange.	After second exchange.	After third exchange.
1	−1·3	−2·0	+4·5	+5·4
2	−1·4	−2·0	+3·2	+3·4
3	−1·5	−2·1	+2·1	+2·0
4	−1·5	−2·1	+1·3	+1·0
5	−1·5	−2·1	+ ·7	+ ·5
6	−1·5	−2·2	+ ·4	− ·7
7	−1·5	−2·2	+ ·1	−1·3
8	−1·6	−2·2	− ·3	−1·7
9	−1·6	−2·2	− ·5	−2·0
10	−1·6	−2·2	− ·7	−2·2
11	−1·6	−2·2	− ·8	−2·4
12	−1·6	−2·1	− ·9	−2·5
13	−1·6	−2·1	−1·0	−2·6
14	−1·6	−2·1	−1·0	−2·7
15	−1·6	−2·1	−1·0	−2·7
Average ...	−1·5	−2·1	+ ·4	− ·6
General average .... = −0·9.				

In precisely the same way the following numbers were obtained in a duplicate experiment:—

During 1st minute.	−2·3	−1·1	+2·7	+3·4
During 8th minute.	−1·6	− ·4	+1·4	+2·2
During 15th minute.	−1·3	− ·1	+ ·7	+1·2
Average of all observations.	−1·6	− ·5	+1·5	+2·1
General average .... = + ·4.				

The mean of this and the preceding experiment gives −·25, an amount evidently quite negligible in comparison with the fluctuations in the value of the net E.M.F. in operation in the several series of observations; and hence indicating that *the* E.M.F. *of a cell set up with zinc- and copper-sulphate solutions of the same strength, amalgamated zinc and electro-copper,* *is really independent of the solution-strength within the limits of observational error.*

Using the same solutions in the same way the following values were obtained, showing that the E.M.F. really does rise perceptibly with the solution-strength when amalgamated copper is substituted for electro-copper, or when electro-zinc is substituted for amalgamated zinc :—

Amalgamated Zinc and Amalgamated Copper.

During 1st minute.	−·5	+15·3	+9·1	+13·0
During 8th minute.	−·7	+ 7·7	+1·3	+ 5·7
During 15th minute.	−·8	+ 5·2	0	+ 3·8
Average of all observations.	−·7	+ 9·0	+2·7	+ 6·5
General average .... = +4·4.				

Electro-zinc and Electro-copper.

During 1st minute.	−1·2	+6·3	+8·2	+7·2
During 8th minute.	+0·9	+4·0	+5·7	+4·4
During 15th minute.	+1·8	+2·9	+3·4	+3·5
Average of all observations.	+ ·3	+4·2	+5·6	+4·8
General average .... = +3·7.				

Electro-zinc and Amalgamated Copper.

During 1st minute.	+5·4	+6·9	+7·8	+11·1
During 8th minute.	+5·4	+5·5	+5·8	+ 8·0
During 15th minute.	+5·5	+4·3	+5·1	+ 5·8
Average of all observations.	+5·4	+5·5	+6·1	+ 7·9
General average .... = +6·2.				

Heat developed during Intermixture of Solutions of Zinc (Copper or Cadmium) Sulphates or Chlorides of different Strengths.

160. The results above described show that when two solutions of different strengths, but containing the same metallic salt, are allowed to intermix by diffusion, plates of the metal contained in the salt immersed in the two solutions respectively acquire different potentials, the potential-difference set up with any given pair of solutions being to some extent dependent on the surface-characters of the plates employed, but being, *cæteris paribus*, greater the greater the difference between the strengths of the solutions, the plates immersed in the stronger solution acquiring the higher potential. It is evident that if there is a development of heat during intermixture of the solutions used, the work done by a current developed on connecting the plates by a conductor may reasonably be supposed to be done in virtue of this heat-development, just as the work done by an ordinary voltaic couple is done in virtue of the heat developed by the chemical actions taking place therein. Accordingly it becomes of interest to determine precisely what amounts of heat are actually generated during intermixture in order to see what relationships hold between the electromotive forces actually generated and those corresponding to the heat-developments.

The required "heats of intermixture" are readily calculable from the values representing the "heats of dilution" obtained by measuring the amounts of heat produced when solutions of metallic salts are diluted to known extents by means of water. If h_1, h_2, h_3 respectively represent the heats of dilution of gramme-molecules of the three solutions $MSO_4\ 2a\,H_2O$, $MSO_4\ 2b\,H_2O$, and $MSO_4(a+b)\,H_2O$ to the same further extent, then H, the heat produced by mixing a gramme-molecule of the first solution with one of the second so as to produce two of the third, is given by the equation

$$H = h_1 + h_2 - 2h_3.$$

In order to obtain the data for the calculation of the various values of H in the case of the solutions examined in the preceding pages, a number of calorimetric determinations were made, substantially in the way described by Julius Thomsen

(*Thermochemische Untersuchungen*, i. p. 18, 1882), using a calorimeter containing 1 litre of fluid in the lower compartment. The quantity of salt employed was usually close upon $\frac{1}{7}$ gramme-molecule, the weight being arranged so that the resulting fluid was of the strength $MSO_4 \, 400 \, H_2O$, or $MCl_2 \, 400 \, H_2O$. The thermometers used were graduated in millimetres, about 11 millimetres representing 1° C.; so that readings being made to $\pm \frac{1}{20}$ millim., the thermometer-error was $\pm \frac{1}{220}$ of 1° C. As determined by means of various blank experiments (with water only intermixed), the limit of accuracy of each experiment was within ± 10 gramme-degrees; so that each observation might be erroneous within the limits of not exceeding ± 70 gramme-degrees per gramme-molecule; but as several observations were usually made and averaged, the probable error of each average was ordinarily within ± 25 gramme-degrees. The following numbers were ultimately obtained as means from upwards of fifty observations, indicating the heat-evolution, in gramme-degrees per gramme-molecule, on diluting $m \, MSO_4 \, 100 \, H_2O$ to $\cdot 25 \, MSO_4 \, 100 \, H_2O$, or $m \, MCl_2 \, 100 \, H_2O$ to $\cdot 25 \, MCl_2 \, 100 \, H_2O$. Plate V. fig. 6 represents the values graphically.

	Zinc sulphate.	Copper sulphate.	Cadmium sulphate.	Zinc chloride.	Cadmium chloride.
$m = 25$......	......	......	......	9000	
20......	....	......	......	8050	
10......	......	......	......	6100	
7......	......	......	1450		
6......	......	......	1075		
5......	375	......	825	4800	100
4......	175	......	625	4400	
3......	100	......	450	3800	
2......	50	50	275	2700	
1·5	Less than errors of observation.	Less than errors of observation.	200		
1			75	1250	
·5			......	400	

161. On calculating from these figures the values of h_1, h_2, and h_3, and hence those of H, for particular cases, it becomes evident that, as a general rule, the E.M.F. corresponding to the value of H falls below the potential-difference actually set up between two plates immersed in solutions of different strengths, the difference being sometimes very considerable. Thus the following tables represent the results thus calculated

when solutions $MSO_4\,2a\,H_2O$ and $MSO_4\,2b\,H_2O$ are intermixed so as to form $MSO_4\,(a+b)\,H_2O$ when $b=200$, and consequently when $h_2=0$. The "observed" values quoted are those obtained with electro-coated plates throughout, save in the case of zinc chloride, where amalgamated plates were employed; all the electromotive forces are expressed in millivolts.

$2a$.	$a+b$.	h_1.	$2h_3$.	H.	Corresponding E.M.F.	Observed E.M.F.	Excess.
Zinc Sulphate.							
20	210	375	0	375	8	27	19
25	212·5	175	0	175	4	22	18
33·3	216·7	100	0	100	2	17	15
50	225	50	0	50	1	13	12
100	250	0	0	0	0	8	8
Copper Sulphate.							
50	225	50	0	50	1	17	16
100	250	0	0	0	0	12	12
200	300	0	0	0	0	6	6
Cadmium Sulphate.							
16·7	208·3	1075	25	1025	23	34	11
20	210	825	25	775	17	28	11
25	212·5	625	25	575	13	23	10
33·3	216·7	450	25	400	9	18	9
50	225	275	25	225	5	14	9
66·7	233·3	200	25	150	3	9	6
100	250	75	20	35	1	4	3
Zinc Chloride.							
4	202	9000	790	8210	181	264	+83
5	202·5	8050	790	7260	160	225	+65
10	205	6100	780	5320	118	149	+31
20	210	4800	760	4040	89	65	−24
25	212·5	4400	750	3650	80	57	−23
33·3	216·6	3800	730	3070	68	52	−16
50	225	2700	700	2000	44	40	− 4
100	250	1250	600	650	14	23	+ 9
Cadmium Chloride.							
20	210	100	0	100	2	32	30
100	250	0	0	0	0	14	14

Analogous results are obtained when the calculations are similarly made for other kinds of mixture: the observed E.M.F. generally notably exceeds that calculated from the heat of intermixture*. It would hence seem that the *modus operandi* of a "diffusion-cell" is to some extent rather analogous to that of a thermo-couple than to that of an ordinary galvanic element, part at least of the energy gained outside the battery being due, not to the heat-development during chemical action taking place, but to the transformation of sensible heat into electric-current energy. It is noteworthy, moreover, that analogous phenomena are presented in cases where strong and weak solutions of acids (*e. g.* nitric and sulphuric) interdiffuse, platinum or other unoxidizable plates being employed: diffusion-cells of this kind are now being examined.

By uniting together in series a sufficient number of diffusion-cells, all the effects of an ordinary voltaic battery can be produced, at least those compatible with the presence of a large resistance in circuit: electrolysis of metallic solutions (*e. g.* copper sulphate) is readily brought about.

Volume-alteration on Intermixture of Solutions of Zinc, Copper, and Cadmium Sulphates.

162. Although not directly connected with the subject of electrical measurement of chemical affinity, it yet seemed of some interest to examine how far the volume-alterations that take place on mixing solutions of different strengths of zinc (copper or cadmium) sulphate run parallel with the thermal developments thereby caused. It might reasonably be anticipated that the much greater heat-evolution taking place on dilution of cadmium sulphate as compared with zinc or copper sulphate would be found to be concurrent with a greater amount of volume-alteration. On examining the matter, how-

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* Since these experiments were made, the third volume of Julius Thomsen's *Thermochemische Untersuchungen* has appeared; in this are given the results of this author's previously unpublished experiments on the heat of dilution of solutions of zinc and copper sulphates, and of zinc chlorides. These figures do not materially differ from those cited above; and their use, instead of those employed in this paper makes no noteworthy difference in the end conclusion that the heat of intermixture usually represents a less E.M.F. than that actually set up in any given case.

ever, this is not found to be the case; the volume-alterations on dilution through a given range being but little different, whichever of the three sulphates be employed, in every case contraction* taking place, even when the solution is already so far diluted as not to cause any measurable heat-evolution on mixing with water.

The observations were made with a large-bulbed dilatometer holding about 94 cubic centim. The volumes corresponding to the various graduations were determined by introducing a known weight of distilled water, and determining the level of the water in the stem—first, when the temperature was a little below 18°·5, the instrument being immersed in a large vessel of water kept agitated; and secondly, when the temperature was a little above 18°·5. In this way the level at 18°·5 was obtained by interpolation. The weight of the contained water (reduced to a vacuum) being known, the volume in cubic centimetres occupied up to the level at 18°·5 was calculated by the formula $V = \frac{W}{\cdot 998602}$; where V is the volume in cubic centimetres, W the weight *in vacuo*, and ·998602 the weight of 1 cubic centimetre in grammes at 18°·5 (Kopp). By making a series of such observations a capacity-table was calculated for the instrument, expressing the volume in cubic centimetres at 18°·5 for each graduation. A known weight of the solution to be diluted was then introduced, and the level at 18°·5 obtained by making observations a little below and a little above that temperature, so as ultimately to obtain the volume occupied by a given weight (reduced to vacuum) of solution. Repetitions of experiments gave values according together within a range of ·00003 (3 milligrammes in 94 cubic centim.), and often within much less; the chief source of discrepancy being in the correction for reduction to a vacuum which was altogether about 100 milligrammes, necessarily varying with the temperature and barometric pressure, so that a small error in temperature or pressure estimation made several milligrammes difference in weight-correction.

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* The rough values obtained in § 106 (Part V.) led to the conclusion that on diluting zinc- or copper-sulphate solution with water an increment in volume takes place. This is now found to be incorrect, the experimental errors of the rough observations being greater than the volume-alterations to be measured.

On the whole, the probable error of the average of some three or four repetitions of an observation was less than ±·00001 (1 milligramme in 94 cubic centim.).

A quantity of the solution to be diluted was then weighed up in a stoppered bottle and a weighed quantity of water added, the weighings being reduced to a vacuum: the whole was thoroughly intermixed, and the weight of a cubic centimetre of the diluted fluid determined as before in the dilatometer; the contraction was then calculated by means of the formula

$$C = \frac{W}{s_1} + \frac{w}{\cdot 998602} - \frac{W+w}{s_2};$$

where C is the contraction in cubic centimetres,

W the weight (*in vacuo*) of solution diluted,

w „ „ of the water added thereto,

s_1 the weight at 18°·5 of 1 cubic centim. of the solution diluted.

s_2 the weight at 18°·5 of 1 cubic centim. of the dilute fluid produced.

The following numbers will serve as an example:—

Temperature.	Dilatometer reading.	Reading at 18°·5.	Cubic centim. corresponding from table of instrument.	Weight of fluid *in vacuo*.	Weight *in vacuo* of 1 cubic centim. at 18°·5*.
17·0	6·25	7·05	94·743	97·671	1·03090
19·7	7·70				
17·0	1·15	1·87	94·556	97·467	1·03088
19·3	2·25				
				Mean	1·03089

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* In the course of these observations the following mean numbers were obtained, representing the weights *in vacuo* at 18°·5 C. of 1 cubic centim. of various solutions $MSO_4\,nH_2O$:—

Copper sulphate.		Zinc sulphate.		Cadmium sulphate.	
n=44·8	1·18725	n=19·06	1·41699	n=15·81	1·59169
75·3	1·11325	19·31	1·41073	18·07	1·52829
109·9	1·078155	21·33	1·376055	18·10	1·52724
174·9	1·049195	32·3	1·25859	32·4	1·31285
276·4	1·03089	49·5	1·17310	49·4	1·21020
462·7	1·01805	98·8	1·088265	95·6	1·11082
		142·8	1·061275	162·9	1·06537
		219·1	1·03980	260·4	1·040795
		422·1	1·020215	424·4	1·02461
		466·0	1·01817		

This solution was made by mixing 53·781 grammes of copper-sulphate solution (of which one cubic centim. was similarly found to weigh 1·18725 gramme) with 232·509 grammes of water (all weights corrected to vacuum), whence

$$C=\frac{53\cdot781}{1\cdot18725}+\frac{232\cdot509}{\cdot998602}-\frac{286\cdot290}{1\cdot03089}=\cdot422.$$

The solution diluted was found by analysis* to contain 16·525 per cent. of anhydrous $CuSO_4$, corresponding with $2\cdot231\,CuSO_4\,100\,H_2O$; hence there was employed altogether $53\cdot781\times\cdot16525=8\cdot887$ grammes of $CuSO_4$, or ·0557 gramme-molecule; so that the contraction per gramme-molecule was $\frac{\cdot422}{\cdot0557}=7\cdot58$ cubic centim., the diluted fluid possessing the composition $\cdot362\,CuSO_4\,100\,H_2O$.

In precisely the same way the following values were obtained on diluting $2\cdot231\,CuSO_4\,100H_2O$ to other extents:—

Solution ultimately obtained, $n\,CuSO_4\,100H_2O$.	Contraction in cubic centimetres per gramme-molecule.
$n=1\cdot328$	2·76
$=\cdot910$	4·40
$=\cdot572$	6·19
$=\cdot362$	7·58
$=\cdot216$	8·88

Similarly the following values were obtained on diluting $5\cdot247\,ZnSO_4\,100\,H_2O$ to various extents:—

$n=4\cdot744$	0·96
$=3\cdot096$	4·78
$=2\cdot020$	7·59
$=1\cdot012$	11·23
$=\cdot700$	12·63
$=\cdot457$	14·03
$=\cdot237$	15·69

And the following, on similarly diluting $6\cdot325\,CdSO_4\,100H_2O$:—

---

* The mode of analysis adopted was to evaporate to dryness a weighed quantity of solution and weigh the residual anhydrous salt after continued heating to 300°–400°, terminating in very gentle ignition for a minute or two at a red heat barely visible in the dark.

Solution ultimately obtained, $n\,CuSO_4\,100H_2O$.	Contraction in cubic centimetres per gramme-molecule.
$n=5{\cdot}534$	1·23
$=3{\cdot}086$	5·86
$=2{\cdot}024$	8·38
$=1{\cdot}046$	11·46
$=\ {\cdot}614$	13·35
$=\ {\cdot}384$	14·98
$=\ {\cdot}235$	15·81

On graphical representation on a large scale and interpolation, the following values are deduced as the amounts of contraction taking place on diluting to the strengths $\cdot 25\,MSO_4\,100\,H_2O$ solutions of strength $n MSO_4\,100\,H_2O$:—

	Zinc sulphate.	Copper sulphate.	Cadmium sulphate.
$n=\cdot 25$	0	0	0
·5	1·8	1·85	1·75
1·0	4·25	4·5	4·0
1·5	6·35	6·4	5·95
2·0	8·0	7·95	7·4
2·25	8·65	8·55	7·95
3·0	10·8	......	9·95
4·0	12·95	......	11·95
5·0	15·05	......	13·75
5·5	16·0	......	14·5

The curves marked respectively 1, 2, and 3 (Pl. V. fig. 7) represent these values. It is evident that the contraction with cadmium solutions is always less than that with zinc- or copper-sulphate solutions, instead of greater, as might have been *à priori* anticipated from the greater heat of dilution. The difference, however, is in no case very great; whilst with zinc and copper solutions the curves almost coincide.

163. From these values the amounts of contraction on intermixture of gramme-molecules of two solutions of any one of the three salts differing in strength are readily calculable by the formula

$$C=c_1+c_2-2c_3,$$

parallel with the analogous equation for heats of intermixture (§ 160); where C is the contraction on intermixture, and c_1, c_2, and c_3 respectively the contractions on dilution to the same ultimate limit of the solutions $MSO_4\,2a\,H_2O$, $MSO_4\,2b\,H_2O$, and $MSO_4\,(a+b)\,H_2O$; and more generally still the contractions are calculable that ensue when any two solutions of any pair of the three salts are intermixed. Thus, when A gramme-molecules of $MSO_4\, mH_2O$ and B gramme-molecules of $M'SO_4\, nH_2O$ are intermixed, the resulting mixture is

$$\left\{ \begin{matrix} M \\ M' \end{matrix} \right\} SO_4 \, \frac{mA+nB}{A+B} H_2O.$$

If, then, *a* be contraction per gramme-molecule on diluting the first solution to the strength of the mixture, and *b* be the (negative) contraction ensuing on (negatively) diluting the second solution to the same strength, the total contraction on intermixture is $Aa+Bb$, and the contraction per gramme-molecule of the two salts used jointly is $\frac{Aa+Bb}{A+B}$. A number of experiments were made which showed that the actual contraction observed was sensibly identical (within experimental error limits) with that calculated in this way, the values of *a* and *b* being deduced from the above table by interpolation. Thus the following values were obtained:—

Different Solutions of the same Salt mixed.

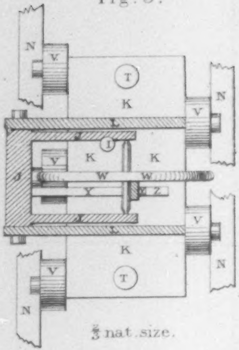
Stronger solution......	$CuSO_4$ 47 H_2O	$ZnSO_4$ 19·3 H_2O	$CdSO_4$ 15·81 H_2O
Weaker solution	$CuSO_4$ 163 H_2O	$ZnSO_4$ 148 H_2O	$CdSO_4$ 171 H_2O
Observed contraction	1·12	3·84	4·88
Calculated "	1·13	3·83	4·66
Difference	+ ·01	− ·01	− ·22

Solutions of different Salts used.

Stronger solution.........	$ZnSO_4$ 19·3 H_2O	$CuSO_4$ 47 H_2O
Weaker solution	$CuSO_4$ 163 H_2O	$ZnSO_4$ 148 H_2O
Observed contraction ...	4·37	·92
Calculated " ...	4·23	·99
Difference	−·14	+·07
$CdSO_4$ 15·81 H_2O	$CdSO_4$ 15·81 H_2O	$ZnSO_4$ 19·3 H_2O
$CuSO_4$ 163 H_2O	$ZnSO_4$ 148 H_2O	$CdSO_4$ 171 H_2O
4·39	4·19	4·41
4·36	4·11	4·42
− ·03	− ·08	+ ·01

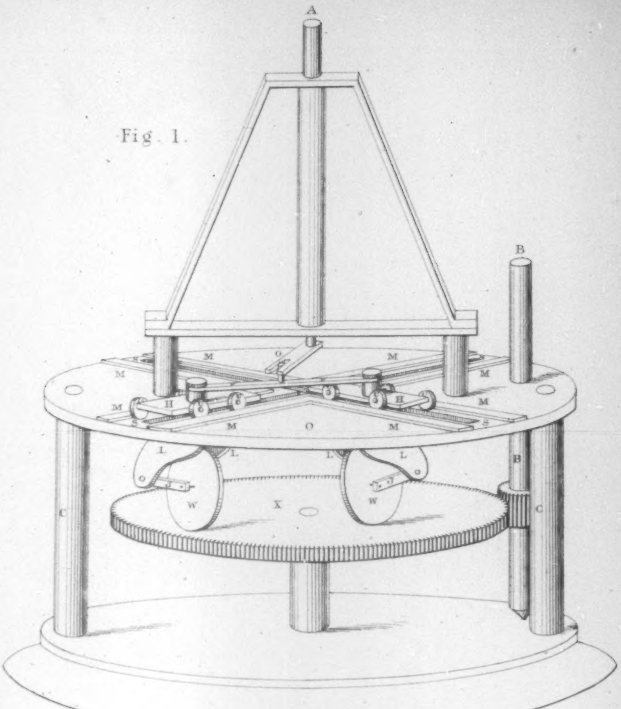
Since but little difference exists between the contractions on dilution through given ranges, whether zinc, copper, or

Fig. 3.


N
V
T
K
L
J
I
W
Y
Z

⅔ nat. size.

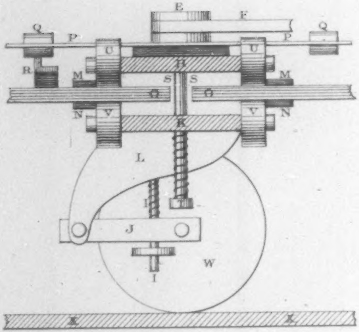
Fig. 1.


A
B
C
M
O
S
H
L
W
X

$\frac{1}{3}$ nat. size.

4

Fig. 4.


E
F
Q
P
P
Q
U
U
R
M
H
M
S
S
O
O
N
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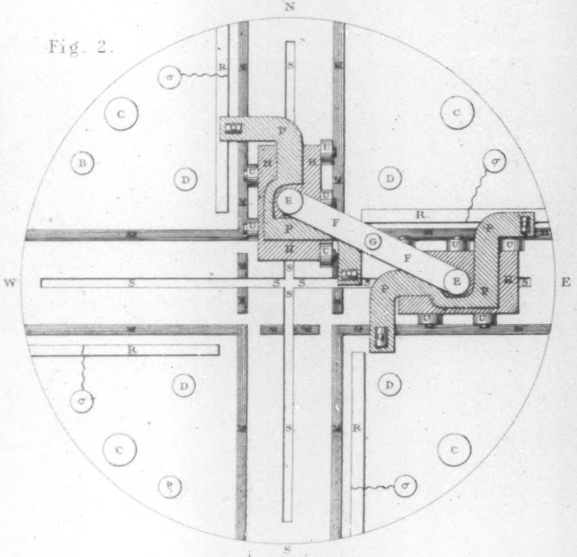
V
N
K
L
I
J
W
I
X
X

$\frac{2}{3}$ nat. size.

Fig. 2.


N
W
E
S
C
C
C
C
B
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D
D
D
σ
σ
σ
σ
R
R
R
R
S
S
S
S
S
S
P
P
P
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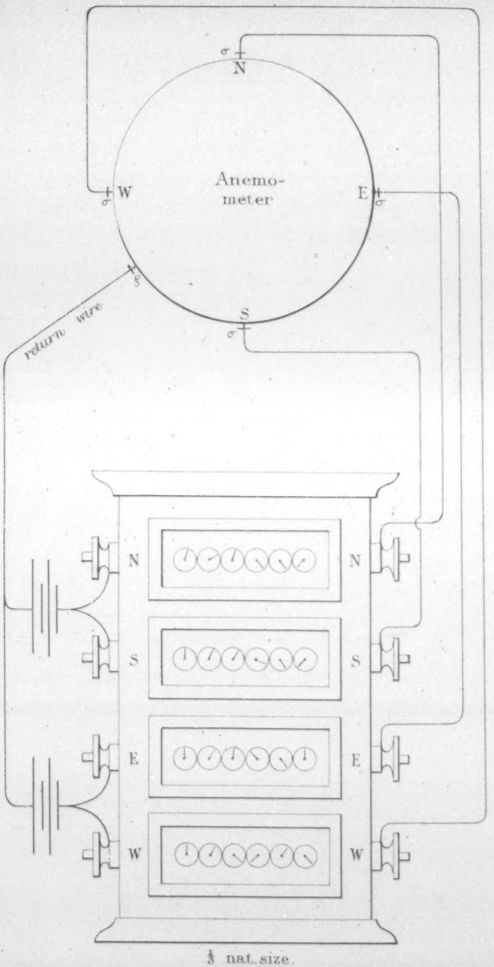
H
H
U
E
E
F
F
G

$\frac{1}{3}$ nat. size.

Minters Bros. lith.


Anemometer
N
E
S
W
σ
σ
σ
σ
ς
return wire
N
S
E
W
N
S
E
W

⅓ nat. size.

Mintern Bros lith.

cadmium sulphate be employed, it results that the amounts of contraction on intermixture when two different solutions of the same salt are mixed will not differ greatly whichever of the three salts be employed. It would hence seem that there is a much closer connexion between the amount of contraction taking place on intermixture, and the potential difference thereby developed, than there is between either of these values and the heat-evolution simultaneously taking place. For varying solution-strengths, the first two values alter fairly concurrently and to extents not widely different, whether zinc, copper, or cadmium sulphate be used. But this is by no means the case with the heat-values, the cadmium value largely exceeding the corresponding zinc and copper values, which latter two are substantially identical.

IX. *On an Integrating Anemometer.*

By WALTER BAILY, *M.A.*[*]

[Plates VI. & VII.]

ON June 10th, 1882, I communicated to the Society a design for an integrating anemometer, and exhibited a working model[†]. I have now to describe the instrument itself, which I have had made by Messrs. Elliott, with the assistance of a grant from the Royal Society. The mechanical part of the instrument is seen in perspective in Plate VI. fig. 1. The base is of iron, and the rest of the instrument is chiefly of brass. On the base stand four columns C, of which only two are shown in fig. 1. These hold a table O, of which fig. 2 gives a view as seen from above. The tops of the columns C are seen in fig. 2. The table supports four columns, D, of which only two are shown in fig. 1, and of all of which the positions are shown in fig. 2. The pillars D hold the supports of a spindle A, fig. 1, which is to be connected with a vane. There is another spindle, B, which is to be connected with Robinson's cups, and which turns, by means of cogs, the large horizontal disk X, so that X will revolve with a velocity which may be taken as proportional to that of the wind. The spindle A carries a horizontal bar G, which is to be kept by the vane in the direction of the wind, and which, by means of a forked end, holds a vertical pin rising from the centre of the bar F. This bar is pivoted at E to the centres of two trucks H, each of which runs by means of five wheels U between tram-lines M placed so as to form a cross with the arms directed towards the cardinal points (compare figs. 1 and 2). The centre of the cross is vertically over the centre of the disk X. Centrally between the tram-lines M are slits S through the table O. The object in having five wheels U placed as shown in fig. 1 (see also fig. 3) is to enable each wheel of the truck H to pass over the slits S, and yet always to keep the pivot E well within the base formed by the remaining four wheels, so that it may be perfectly steady. On the underside of the table O are similar tram-lines, N; and trucks K run in these tram-lines, each on five wheels, V. Fig. 3 shows one of these trucks seen from below, with portions of the tram-lines N.

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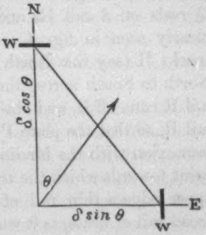
[*] Read December 8, 1883.

[†] Phil. Mag. Sept. 1882; Phys. Soc. Proc. vol. v. p. 157.

Fig. 4 is an elevation showing an end view of the trucks H and K, with a portion of a section of the table O across a slit S. Two rods, T, of which the ends are shown in fig. 3, and of one of which a side view is shown in fig. 4, are rigidly connected with H and pass through the slit S and through holes in K. Spiral springs surrounding the rods T and resting on the heads of the rods press K upwards, and make it keep its position exactly and firmly under H. Each truck, K, carries firmly fastened to it two pieces of brass, L (see figs. 1, 3, 4); and between these pieces is pivoted a bar with arms J, and between these arms is pivoted a wheel W, which is carried in a vertical position also at right angles to the slit through which T passes. A rod I connected with K is surrounded by a spiral spring which presses on J, and so keeps a steady pressure between the wheel W and the disk X. The pivots of J and W are so placed that, when W touches X, these pivots all lie in one horizontal plane, and the point of contact of W with X is vertically below the centre of the pivot E (figs. 1, 2).

Now suppose the wind to lie between North and East, and the direction from which it blows to make an angle θ with North. Let Ω be the velocity of the wind. Then the resolved parts of the wind towards North and East will be $\Omega \cos \theta$ and

$\Omega \sin \theta$ respectively. But if δ be the length of the bar F (fig. 2) measured between the centres of its pivots E, it is easily seen, from the diagram in the margin, that the distances of the wheels W from the centre of the disk X (fig. 1) are $\delta \cos \theta$ and $\delta \sin \theta$ towards the North and East respectively. Now the speeds of the wheels W are proportional to the speed of the disk X on which they roll multiplied by these distances, and the speed of the disk X is proportional to the velocity Ω of the wind. Hence the speeds of the wheels W are proportional to $\delta \cos \theta . \Omega$ and $\delta \sin \theta . \Omega$ respectively; that is, they are proportional to $\Omega \cos \theta$ and $\Omega \sin \theta$, which are the resolved parts of the velocity of the wind.



If, now, we were to add a mechanical counter to each of the wheels W, the increase of the readings of these counters would give the integral of the resolved parts of the wind towards the North and East; and inasmuch as the wheels W revolve in the contrary direction when they have passed across the centre of the disk X, South winds would act on the counters as negative North, and West winds as negative East. Two counters would be sufficient, as a preponderance of South wind would be indicated by a decrease in the reading of the North counter, and a preponderance of West wind by a decrease in that of the East counter.

It was found, however, much more convenient to make each wheel W complete an electric circuit at each revolution, and to use an electric counter; but inasmuch as such a counter will not distinguish in which direction the wheel is turning, it was necessary to have separate counters for North and South, and to shunt the circuit from one counter to the other as the wheel W crossed the centre of the disk X, and to make a similar arrangement for East and West.

I will now describe the electric system adopted:—Parallel with the tram-lines M (fig. 2) are insulated rails R, one of which is seen in section in fig. 4. Each rail, R, is connected by an insulated wire with an insulated binding-screw σ. Each truck, H, bears a thin insulated plate of brass, P, seen in face in fig. 2 and edgeways in fig. 3; and each end of the plate P carries a small wheel, Q. At any moment, except when the truck is passing the centre of the cross, one of the wheels Q rests on a rail R, and the other is in the air. This is clearly seen in fig. 4. At the moment when one of the trucks H (say the North and South one) passes, say, from North to South across the centre, the wheel Q on the North rail R runs off it, and the other wheel Q runs on to the South rail R, so that the plate P of the truck is always in electrical connexion with the binding-screw σ belonging to the cardinal point towards which the truck lies. The rails R have for their upper edge a thin rail of platinum. This was added to the broad rail of brass, as it was found that points of dust or corrosion sometimes made accidental breaks in the electrical contact between R and Q. In the truck K which runs below H are two parallel tongues Y, Z, very near one another (see fig. 3, in which the full length of Y is seen, but only the end of Z). Both are fixed to J; but Z is also insulated from J, and is connected by an insulated wire, which passes through the slit S (fig. 4) and through a hole in H, with the insulated plate P. The tongue Y is electrically connected with K, and so through various points of contact with the table O. There is a projection from the axle of the wheel W (fig. 3), which once in every turn of the wheel pushes against the tongue Y and brings it into contact with the tongue Z. On the table O (fig. 2) is another binding-screw ρ, which is not insulated. Now suppose a truck H to be upon the North arm of the cross. Its tongue Z is in electric connexion with the North binding-screw σ, and the whole of that part of the system is insulated from the table O. Every time the wheel W turns round, contact is made between Y and Z; and the effect is that the North σ is put into electrical connexion with the table O, and therefore with the binding-screw ρ. The general electrical system is shown in Plate VII., which gives a front view of the box of counters, and a diagram of the anemometer, batteries, and wires. The box contains four counters lettered according to the cardinal points, and from the binding-screws on one side (the right in the figure) insulated wires pass to the corresponding insulated binding-screws σ on the anemometer. From the binding-screws on the other side of the box of counters insulated wires also proceed. The North and South wires are connected with one pole of a battery, and the East and West wires are connected with the same pole of a similar battery. The other poles of the batteries are connected by a wire which returns to the anemometer to the uninsulated binding-screw ρ. If more convenient, the return wire may of course be omitted, and the batteries and anemometer be connected to earth.

Let us now suppose the wind is blowing from about North-east. The trucks H, K are now on the North and East arms of the cross. The circuit through the South counter is complete from the tongue Y through the table O, the return wire, the South counter, and then to the South binding-screw σ and South insulated rail R; but there it stops, and no current can therefore pass through the South counter. The west circuit is stopped in a similar manner. But in the case of the other circuits, the insulated rail R is in contact with the wheel Q, and so through P the circuit is carried on as far as the tongue Z. Hence in the circuits through the North and East counters a current passes whenever the corresponding tongues Y and Z are pressed together, and the corresponding counter marks *one*.

To determine the value of the readings of the counters, we may resort to measurements of the instrument or to direct experiment. If we place one truck at its furthest distance from the centre and rotate the spindle B a certain number of times, and then note the increase in the reading of the corresponding counter, there will be found a constant ratio k between them, so that an increase of n on the counter denotes kn revolutions of B.

Letting δ, as before, be the length of the bar F between its points E (fig. 2), δ is the greatest distance which the wheel W can go from the centre. Put ϵ for the radius of W, ζ for the number of cogs on the edge of the disk X, and η for the number of cogs on the spindle B; we have

Speed of X : speed of B $=\eta : \zeta$,
„ W: „ X $=\delta : \epsilon$,
„ W: „ B $=\delta\eta : \epsilon\zeta = 1 : k$,

which gives us $k=\dfrac{\epsilon\zeta}{\delta\eta}$.

If we place the arm G in any other position and turn the spindle B for some time, and then read p and q as the increase in the readings of the counters of the adjacent cardinal points, the resultant reading for magnitude is $\sqrt{p^2+q^2}$, and the number of revolutions of B will be $k\sqrt{p^2+q^2}$, where k has the same value as before. The direction of the bar G may be determined by taking θ as the angle between the bar and the cardinal point to which p relates. Then

$$p : q = \cos\theta : \sin\theta;$$

whence

$$\tan\theta = \frac{p}{q}.$$

Of course if B is rotated a certain number of times (say 500), the value of $\sqrt{p^2+q^2}$ must be the same in whatever position G has been fixed throughout the experiment.

By repeating this experiment with different positions of G, we get a means of testing the amount of error to which the instrument is liable.

When the anemometer is connected with a vane and with Robinson's cups, let us suppose the wind to remain in one direction for some time; or, if that cannot be secured, let us either tie up the vane, or disconnect it from the spindle A and fasten the spindle. Let l revolutions of the cups indicate one mile of wind, and m revolutions of the cups give one revolution of the spindle B. Let p and q be the readings of the counters, then the miles of wind indicated will be

$$k\sqrt{p^2+q^2}\cdot\frac{l}{m}.$$

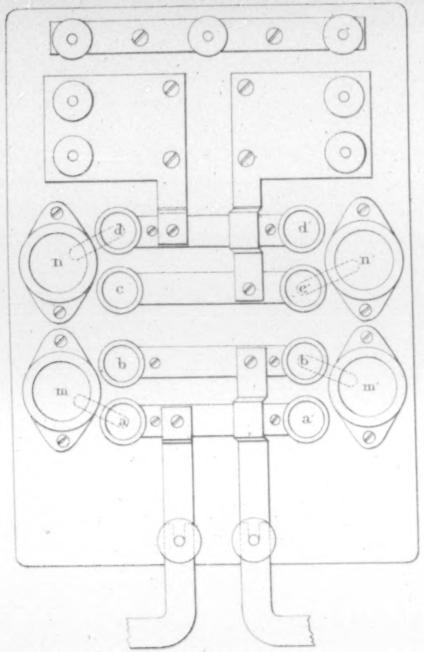
In ordinary use the bar G will be shifted about in all directions by the wind, and we may have an increase in the readings of all the counters; let these be represented by n, s, e, w for North, South, East, and West respectively; then the resultant transfer of air during the interval since the last reading will be

$$k\sqrt{\{(n-s)^2+(e-w)^2\}}\frac{l}{m};$$

and its direction measured from North towards East will be given by the equation

$$\tan\theta = \frac{e-w}{n-s}.$$

Fig. 2.


d
d'
n
n'
c
c'
b
b'
m
m'
a
a'

½ nat. size.

Fig. 3.

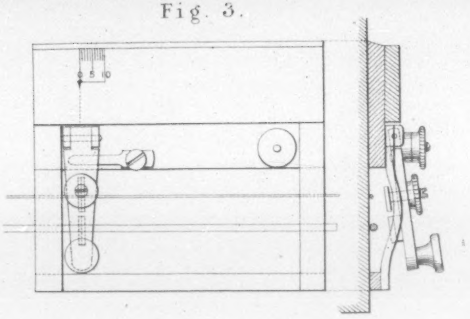


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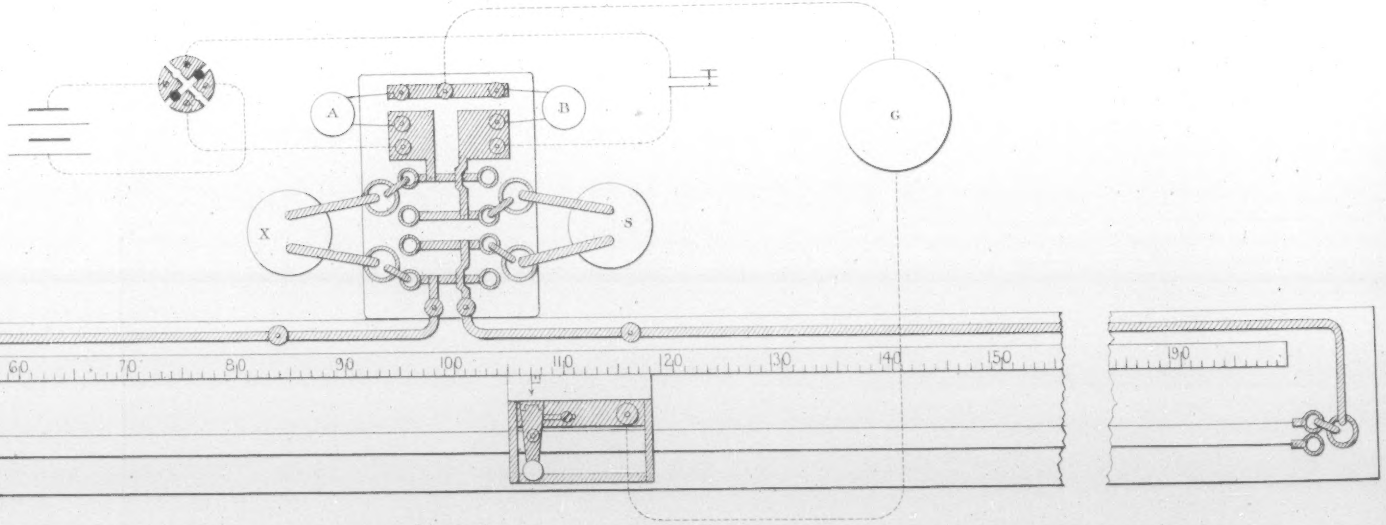
Fig. 1.


A
B
G
X
S
10
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190

⅓ nat. size.

Mintern Bros. lith.

X. *On a Modified Resistance-Balance.*

By Professor Silvanus P. Thompson, *B.A., D.Sc.*[*]

[Plate VIII.]

Several forms of Resistance-Balance modified for the purpose of facilitating the accurate measurement of small resistances or small differences of resistance are known. The modification due to Prof. Fleeming Jenkin[†], and the Double-bridge of Sir W. Thomson[‡] are perhaps the earliest and least-known of these. Kirchhoff's arrangement, as further modified by Matthiessen, is well known under the name of the "divided-metre" bridge. The method of using this form of balance suggested by Professor G. Carey Foster[§], in which the difference between two nearly equal resistances is expressed directly in terms of a length of a graduated wire whose resistance is very accurately known, is so extremely reliable, that probably no one who once adopts this method of testing resistances will ever go back to the cruder and less accurate methods. The essence of the method lies in arranging the coil whose resistance is to be measured and the standard coil to which it approximates in series with the graduated wire, in such a manner that the positions of the two coils can be interchanged. The points of the wire at which the potential is the mean between the potentials at the two ends of the series having been determined, both before and after the interchange, the resistance of the length between these two points is the desired difference. A special modification of the balance for facilitating Foster's method was described to the Physical Society in Dec. 1879 by Dr. J. A. Fleming[‖]; and has been since then systematically used in the Cavendish Laboratory by the Committee on Electrical Standards for the comparison of standard coils. Although extremely convenient, Dr. Fleming's Balance appears to me to be open to several objections. In the first place, the interchange of the two coils, though much more easily accomplished than in the older divided-metre form, is effected by lifting the terminals of each coil out of one of two pairs of mercury-cups, and removing them to the other pair. This operation is not convenient in certain cases, as, for example, when the resistance is being taken of a wire heated in an oil-bath to various successive temperatures, or when some contact-resistance is to be measured which must on no account be shaken. Again, in Fleming's Balance the graduated wire is bent into a circle and laid in a groove, contact being made by a trigger attached to an arm, pivoted at the centre of the circular wire. This arrangement, though I have heard no complaint of its practical efficiency, is open to two objections. It must be much more difficult to lay the wire with an even stress at all points than is the case with a straight wire stretched between two points. The range of resistances measurable by this bridge is limited to something less than the actual resistance of the graduated wire. Lastly, a circular scale having about 300^{c} divided into 1000 parts is not so easily obtained as a straight metre-scale.

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[*] Read February 23, 1884.

[†] Report of Committee on Electrical Standards.

[‡] Proc. Roy. Soc. vol. xi. p. 313 (1861).

[§] Proc. Soc. Telegr. Engin. vol. i. pt. 2, p. 196 (1872).

[‖] Proc. Phys. Soc. vol. iii. p. 174; Phil. Mag. ser. 4, vol. ix. p. 109 (1880); Telegr. Journal, vol. viii. p. 3 (1880).

I have therefore designed a form of resistance-balance which meets the desiderata. It consists of two parts—a divided wire or rheocord, and an arrangement of mercury-cups, connecting-pieces, and terminals to be attached at the back of the rheocord part. The figure 1, Plate VIII., shows the general arrangement of these two parts; the connexions between the two parts being made by strips of copper 3 millim. thick, secured under clamping-screws. X is the coil whose resistance is to be measured, and S the standard coil. The terminals of each of these coils dip into two large mercury-cups turned in solid copper; these are shown half size in fig. 2, and are marked $m\,n$ and $m'\,n'$ respectively. Between these cups lie four parallel bars of solid copper $a\,a'$, $b\,b'$, $c\,c'$, and $d\,d'$, the ends of which terminate also in mercury-cups. The bars $a\,a'$ and $b\,b'$ communicate by stout copper connexions with the two ends of the rheocord part. The other two bars communicate with the battery terminals and with the terminals for the two balanced coils A and B. In all accurate tests these coils should be approximately equal to the X or S, and should be very nearly equal to one another.

As they are not required to be interchanged, they are simply clamped with copper connexions under flat-headed terminal screws. Short stout pieces of copper, amalgamated at the ends, serve to connect the mercury-cups as shown in fig. 1, m being connected with a, n with d, m' with b', and n' with c'. The connexions being thus made, an observation is taken, and the distance x along the scale of the point of contact with the galvanometer-circuit is recorded. Then the connexions are altered, m being placed in communication with b, n with c, m' with a', and n' with d'. This has the same effect as if X and S were bodily interchanged; and without lifting either of those coils as in Fleming's instrument. Balance having been once more obtained, and a new reading x' of the scale having been taken, the length $x-x'$, multiplied by the resistance per centim. of the divided wire, is equal to the actual difference between X and S.

The switch-board part is made of such dimensions that it can be attached on to any of the ordinary pattern of metre-bridges. The ordinary metre-balance is, however, limited in its application, so far as Foster's method of comparison is concerned, to the comparison of resistances which do not differ by a greater amount from one another than the actual resistance of the wire of the rheocord part. To facilitate the comparison of coils of high resistance whose resistances differ by several ohms, I have adopted the following arrangement of the rheocord part. Two wires are selected, each two metres long, one having a resistance of about a quarter of an ohm, the other from eight to ten ohms. They are stretched parallel upon a board 213 centim. in length, provided with a two-metre scale, which should be divided into millimetres. Either of these wires can be used at will, connexion being made to either at one end of the bridge by a stout copper link dipping into mercury-cups drilled in the wood and lined with copper. Stout copper rods of about 1 square centim. section lead from the ends of the stretched wires to the screws, by which the switch-board part is connected with the rheocord part. The galvanometer-contact is made by means of a sliding key shown separately in fig. 3, which is provided with a vernier, and which by a simple arrangement can be set so as to make the contact with either the thick or the thin wire, as may be desired. In the instrument exhibited to the Society the stout wire is of german-silver 2·1 millim. in diameter, and of 0·2385 ohm resistance. The thin wire is of silver-platinum alloy; its diameter is 0·33 millim., and its resistance 8·21 ohms. The form of slider adopted is a much more well-conditioned arrangement than the usual heavy medal sliding key standing on three legs, and is more convenient in practice. The greater length of rheocord, though it renders the instrument less portable, increases the range of the instrument without affecting its sensitiveness.

XI. *On Eutexia.* *By* FREDERICK GUTHRIE*.

VII.

INTRODUCTION.—Although this memoir does not treat directly of the relationship between water and salts, the subject is so analogous with that examined in my memoirs on "Salt-Solutions and Attached Water," that I have numbered the paragraphs in sequence with those of memoir VI. on that subject (Proc. Physical Society, vol. ii. p. 291).

The main argument of the present communication hinges upon the existence of compound bodies, whose chief characteristic is the lowness of their temperatures of fusion. This property of the bodies may be called Eutexia †, the bodies possessing it eutectic bodies or eutectics (εὖ τήκειν). It is at once apparent that the cryohydrates are essentially eutectic. It will, however, perhaps be better to make the term more useful by limiting its application. I shall use it, and I should like it to be used by others, for bodies made up of two or more constituents, which constituents are in such proportion to one another as to give to the resultant compound body a minimum temperature of liquefaction—that is, a lower temperature of liquefaction than that given by any other proportion. Here, again, the cryohydrates completely satisfy the definition. But it will be shown that they constitute only one term of a series; that their melting or liquefaction is quite continuous with the so-called fusion of mixed metals or salts; and that the eutectic alloys of metals, many of which have been long imperfectly known, and the eutectic alloys of salts, which I shall describe (§§ 207–229), are the perfect homologues of the cryohydrates. Let me, in a word, invite my readers, while looking upon water as fused ice, to trace the analogy between the behaviour towards solids of water on the one hand, and some other fused substance on the other.

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* Read May 24, 1884.

† Used in very much this sense by Aristotle. I should have preferred the word hypolytic; but I am instructed that, although sanctioned by its use in Chemistry, this employment of ὑπό is not strictly admissible.

Eutectic Metallic Alloys.

§ 195. Metals mix with one another in various proportions forming Alloys, many of which are in extensive use in the arts. Amongst the most instructive aspects of alloys is certainly that which results from a comparison of the properties of the alloy with those of its constituents. And, further to specialize, the discussion of the relation between the temperature of fusion of the mixed metal and the temperatures of fusion of its elements forms a chapter of the highest significance.

§ 196. In studying this chapter, I employ Bismuth as one of the elements on account of its low melting-point, and because it can be got very pure. Fused bismuth will be the homologue of the water or fused ice of my previous memoirs, and the metal with which it forms alloys will be the homologue of the salt. The bismuth used in the following experiments melted at 263° C.

§ 197. *Bismuth and Zinc.*—It has been asserted that when bismuth and zinc are melted together two alloys are formed which do not mix, the upper being an alloy of 2·4 bismuth and 97·6 zinc, and the lower of from 8·6 to 14·3 bismuth and from 91·4 to 85·7 zinc (see § 206). Such a condition and such a ratio may accidentally exist; but is only occasional. Let bismuth be fused and heated to about 350°, and let as much melted zinc be added in small quantities at a time as the bismuth will form a liquid alloy with at about that temperature. Let now the temperature be watched until it has sunk to about 250°. The liquid is run off and a little bismuth is added to the contents of the crucible, which is heated until fusion ensues, and a second amount of liquid at 250° is again obtained. This and the quantity obtained by the first process are melted together and allowed to cool gradually. The temperature sinks almost immediately to 248°, and remains constant at that temperature. The alloy maintains the same temperature to the very last, and is the eutectic alloy of these metals. It showed on analysis :—

	Per cent.	Melting temperature.
Bi	92·85	248°.
Zn	7·15	

Of course this eutectic alloy is now to be made by melting the metals together in the above ratio ; but on account of the oxidation of the zinc at about its melting-point, it is better to provide a little excess of that metal and to remove the excess by the above method.

§ 198. *Bismuth and Tin.*—In forming the eutectic alloy of these, the bismuth need be only just fused. A roll of tin foil is stirred into the bismuth, and in spite of the cooling effect, the alloy which is formed remains liquid. When the temperature reaches about 150°, the roll of tin is withdrawn, and the temperature is watched as the alloy cools. The temperature ceases to fall at 133°, which is the fusion temperature of this eutectic alloy. Having satisfied oneself of this, the whole may be remelted, and about a quarter having been allowed to solidify at 133°, the rest is poured off, and is pure. This alloy is very finely crystalline when quickly cooled; it is very brittle and its freshly broken surface closely resembles that of cast iron. It showed on analysis :—

	Per cent.	Temperature of fusion.
Bismuth	46·1	133°.
Tin	53·9	

§ 199. *Bismuth and Lead.*—Proceeding in a very similar manner as with tin, a fixed temperature of 122°·7 is reached. This eutectic alloy has the composition :—

	Per cent.	Temperature of fusion.
Bismuth	55·58	122°·7.
Lead	44·42	

It is of a bluish grey, is malleable and easily cut or sawn.

§ 200. *Bismuth and Cadmium.*—On adding melted cadmium to melted bismuth and proceeding as above, it is possible to obtain an alloy whose melting-point is 144° C. It shows, on analysis, the following composition:—

	Per cent.	Temperature of fusion.
Bismuth	59·19	144°.
Cadmium	40·81	

§ 201. So that we have the following results:—
Eutectic alloy of Bismuth with

		Per cent.		
Lead	contains	44·42 lead	and melts at	122°·7
Tin	„	53·90 tin	„	133
Cadmium	„	40·81 cadmium	„	144
Zinc	„	7·15 zinc	„	248

These weight-ratios are none of them simple atomic weight-ratios. Of course, in many cases, metals can be fused together in simple multiples of their atomic weights, but in most such cases, on cooling the alloy, one of the metals will separate out first and so destroy the ratio. In other cases an alloy richer than the original alloy in regard to one of the metals, and therefore a homologue of a subcryohydrate, separates, and the original ratio is again disturbed. When we are dealing with metals which, like antimony or arsenic, on the one hand, are themselves halogenous, or with such strongly chemico-positive metals as sodium on the other, we may and do get alloys of atomic composition—metallo-metallic salts. But the temperatures of fusion of these are never, as far as I am aware, lower than that of either (both) of the constituents. They are not eutectic. Nor is it easy to see any reason whatever why they should be so. On the contrary, we should expect such an alloy to be soluble in one or other of its elements, with depression of temperature. The statement therefore that alloys of minimum melting-points are got on mixing the metals in certain simple ratios of their atomic weights, is presumably to be put on one side. As the cryohydrate forms itself when a salt-solution of any strength loses heat, so the eutectic alloy forms itself when an alloy whose constituents are in any ratio is cooled. The only exception to this is when the constituents are in the ratio homologous with that between the constituents of the subcryohydrate. So-called "fusible alloys," or "fusible metals," are imperfect eutectic alloys. And it is seen that the melting-points obtained by previous experimenters with bismuth-tin and bismuth-lead are considerably higher than those above shown (see also § 206).

§ 202. Further, if we take the eutectic alloy of bismuth-tin and that of bismuth-lead, and treat them together as though they were single metals, we get the eutectic alloy of the three metals; or either of these alloys with bismuth-cadmium gives a corresponding tri-eutectic.

These and certain other tri-eutectic alloys may form the substance of a further communication. They stand in the closest connexion with the cryohydrates of mixed salts, which were discussed in §§ 109–116.

§ 203. Again, a tetra-eutectic is obtained either by building up from the tri-eutectic and a metal, or from three eutectics; or perhaps more readily, although with greater waste of metal in the first tentative experiment, by fusing the four metals together. The three eutectic bismuth alloys above described were fused together in considerable quantity and in indefinite ratio. As the mass had only partly solidified at 100°, it was pressed in a linen bag under boiling water. The liquid portion was further cooled. A large amount remained liquid at 71° C.; at which temperature the thermometer thenceforth stood until the whole was solid. On remelting several times, and collecting that which remained liquid after about a fifth had solidified, the eutectic alloy of bismuth-tin-lead-cadmium was obtained pure. It showed the following composition:—

Bismuth	47·45	47·38
Lead	19·39	19·36
Cadmium	13·31	13·29
Tin	20·00	19·97
	100·15	100·00

The question, very interesting to mineralogists, immediately arises, Can a tetra-eutectic alloy be made without loss by mixing three dieutectic alloys in some proportion with one another? The answer is in this case certainly in the negative.

For according to § 199, 19·36 of lead require 24·25 of bismuth. Again, according to § 200, 13·29 of cadmium require 19·27 of bismuth, and according to § 198, 19·97 of tin require 17·08 of bismuth. So that to satisfy the three metals lead, cadmium, and tin eutectically, 60·52 of bismuth would be required, instead of 47·45.

The above alloy is extremely closely grained and brittle. It may, however, be bruised and rolled. It takes a high polish. When in some thickness its fracture is conchoidal, exposing steel-grey surfaces. This highly eutectic alloy may find uses in the arts, as with the exception of alloys containing mercury and those of potassium and sodium, it has a melting-point lower than any alloy before described.

§ 204. The above experiments, in which bismuth replaced the ice of my previous experiments with salt-solutions and some other metal replaced the salt, are of course only a few of an innumerable series of series. But they will serve to show the genesis of bodies of this class. I have already* pointed out how the "de-leading" of the lead-silver alloy in Pattinson's process is really analogous to the separation of ice from a salt-solution. The residual liquid alloy should have a composition analogous to that of a cryohydrate, and should be the eutectic alloy of lead-silver. If this be so, its temperature of fusion should be lower than that of lead itself; and that it is so is proved by the separation of solid lead from the melted mass. It is well known that Pattinson's process may be "pushed too far." According to the above interpretation, this simply means that when the fusion-temperature of the eutectic alloy is reached, this body solidifies as a whole and is raked away as the lead had been. A pyrometer, an air thermometer, in the mass would be an absolutely trustworthy guide as to the proper time for cupellation to replace "de-leading."

§ 205. That certain metals may and do unite with one another in the small multiples of their combining weights may be conceded. To such bodies the eutectic alloys bear the same relationship as the cryohydrates bear to the common hydrates, and, like the latter bodies, their constituents are not in the ratio of any simple multiples of their chemical equivalents. But their composition is not, on that account, the less fixed, nor are their properties the less definite. Many of these eutectic alloys have been known in partial purity for ages, having been nearly reached by repeated trial or by assuming a molecular ratio. But they have not been recognized as a class numbering merely as dieutectics several hundred (say 1700), which can be obtained, as above shown, systematically and in a state of great purity. Nor does the fact that several instances are known in which metals combine with one another in the chemical sense—that is, in simple multiple ratio by weight of their combining weights and with liberation of heat—at all diminish the possible number of such eutectic alloys. For, firstly, as a salt may unite with water, as when anhydrous chloride of calcium does so, to fix the water as crystalline water, and also may unite with water as a cryohydrate, so two metals may unite in one proportion while they form a definite eutectic alloy in another. Secondly, the very bodies resulting from the chemical union of the two metals will possibly, and probably, furnish starting-points of new series of eutectic alloys, consisting of a single metal on the one hand and the chemical alloy on the other.

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* R. Inst. Lecture, Feb. 16, 1877.

§ 206. It will be instructive to compare the results given above with results obtained by some previous experimenters who have examined bismuth alloys.

According to Rose, one part by weight of lead, one of tin, and two of bismuth melt at 93°·75. That a part of it may melt, and so the whole soften at that temperature, need not be questioned. But that the whole should melt from first to last at any fixed temperature, is so highly improbable as to be practically impossible on account of the simplicity of the proportion.

According to Matthiessen and v. Bose zinc and bismuth form two alloys, one containing 97·6 of zinc, and the other from 8·6 to 14·3 (instead of 7·15), which two alloys are immiscible. The melting-points do not appear to have been given. Indeed, as neither of these is eutectic, so neither has a proper melting-point.

The nearest approach to an eutectic alloy appears to have been made by Rudberg, who, on melting together 177 parts by weight of tin, and 213 of bismuth (tin =45·38 per cent., bismuth =54·62 per cent.), obtained an alloy which is said to have a constant melting-temperature of 143°. Rudberg further states that all other ratios have higher melting-points, and that, on cooling, the liquid portion reduces itself to this ratio. The above ratio is intended for that between three "atoms" of tin and two of bismuth. For if the atomic weight of tin be 118 and that of bismuth 210 (Rudberg takes tin 56, bismuth 106·5), we should have in Sn_3Bi_2 the percentage, tin =45·74 per cent., bismuth =54·26 per cent. It has been shown above that the true eutectic alloy has a melting-point 10° lower than Rudberg's, and the composition, tin=53·9, bismuth =46·1 per cent.

Again, it is stated that when lead and bismuth are fused together, in the proportion of three atoms of lead to two of bismuth, an alloy is obtained whose melting-point is constant at 129°. This ratio requires lead 42·49, bismuth 57·51 per cent. The true eutectic alloy has a melting-point 6°·3 C. lower, and, as we have seen, has the composition, lead 44·42, bismuth 55·58.

The preconceived notion that the alloy of minimum temperature of fusion must have its constituents in simple atomic proportion,—that it must be a chemical compound,—seems to have misled previous investigators. Such misconception could scarcely have arisen if the existence and properties of the cryohydrates had been known.

§ 206 A. It was shown many years ago (about 35) by my brother Francis, that if two counties are only then supposed to be in contact when they have linear common boundary, to colour a map so that no two counties in contact shall be coloured alike, four colours at most are needed. Taking the special case in three dimensions it is clear that five, but no more spheres, may touch one another (each touching all). If there be such things as atoms, and if they be spherical or of one curvature, not more than five can touch, each touching all. Chemical compounds are known containing more than five elements. But this circumstance does not obliterate the limit of the eutexia of alloys, which are neither atomic nor molecular.

Salt Alloys.

§ 207. It cannot be gainsaid that, vast as is the importance in the arts of the elementary metals and their alloys, yet in terrestrial nature the interaction and relationship of compound bodies is at least of equal importance, and of far wider scope; for the science of such interaction and relationship constitutes the greater part of chemistry and petrology.

Amongst the non-metallic elements we should expect the class analogous with the eutectic alloys to be very restricted in number, on account of the chemical attitude of such elements towards one another, that is their tendency towards chemical union.

Chemical compounds, however, all of which may for brevity's sake be called salts, can give rise to an indefinite number of eutectic bodies; indeed to an indefinite number of series of such bodies. The whole of the preceding memoirs on Salt-solutions and Attached Water are in fact mainly a study of one such series. The cryohydrates are nothing else than eutectic alloys of the one salt called water with the various other salts. If instead of fused ice (water) we employ another fused salt, say fused table salt, we may expect to find it forming eutectic alloys with other salts, whose characteristic should be fusibility at a temperature lower than that of either (both) of its constituents.

§ 208. In choosing salts whose behaviour under such examination shall be as free as possible from ambiguity we must avoid :—

First, those which are decomposed when heated by themselves to anything like the temperature to which they are to be exposed in the experiment. And we are safe in this respect, if we confine ourselves to those which are not decomposed on fusion. For the bodies we are seeking should have temperatures of fusion below the temperature at which that one of its constituents fuses whose temperature of fusion is the lower of the two—it should be eutectic.

Secondly, must be avoided those which react on one another chemically, either in the sense of suffering double decomposition, or in that of direct combination whereby double salts are formed. It will be shown in § 225–227 that it is not always necessary to avoid the first of these contingencies. The possibility of double decomposition is of course avoided when the two salts used have either a common basic, or a common acid constituent.

Thirdly, are to be eschewed those salts which attack at high temperatures the vessels employed.

Amongst all salts perhaps Nitre answers these requirements best, as the body whose homologue is ice in the previous memoirs of Salt-solutions and Attached Water. Nitrates do not form double salts with one another, nor with other salts (compare, however, Karsten). Nitre may be raised without suffering decomposition to a temperature far above its temperature of fusion; possessing in this respect a wider range of available temperature than nitrate of ammonium, which might otherwise be preferable on account of its lower melting-point.

§ 209. In the following paragraphs, from § 210 to § 227, temperatures up to 280° C. were measured by means of a mercurial thermometer. Those above that range were determined by an air-thermometer with a horizontal stem about three feet long. The index was a plug of mercury. The total range was from about 0° to 380° C. As most of the experiments in which the air-thermometer was used were made on days on which the barometric pressure was nearly the same, no correction was needed. On other days the air-thermometer was standardized at the temperature of boiling water, with the mercurial one placed by its side in the water.

§ 210. *Nitre.*—I find that the temperature of fusion of pure nitre is 320° C.

§ 211. *Nitre and Chromate of Potassium.*—If nitre be fused in a large porcelain crucible and neutral chromate of potassium be added, some of the chromate is dissolved. The higher the temperature the larger the quantity. On suffering the solution to cool slowly, chromate of potassium separates out in fine powder, which sinks through the fused mass. The temperature falls till it reaches 295°, at which it remains constant; and the liquid begins to solidify. The liquid portion is poured into a fresh crucible; and this may be repeated any number of times. The temperature of solidification is constant. The liquid being poured upon a cold slab solidifies to a mass, which has when cold precisely the colour of sulphur. Of this alloy 2·4881 grams gave 0·1226 chromate of barium. This corresponds to 0·0936 chromate of potassium, which is 3·76 per cent. Accordingly this alloy is:—

		Melting-point.
Nitre	96·24	295°.
Chromate of potassium .	3·76	

§ 212. *Nitre and Nitrate of Calcium.*—The three metals calcium, strontium, and barium promised to be of interest in furnishing nitrates alloyable with nitre. The method of experiment was precisely as before, the nitrates having been rendered anhydrous before they were added to the fused nitre. The bases were all separated and weighed as carbonates.

The eutectic alloy of nitre with nitrate of calcium has a melting-point of 251°. Of this, 1·8300 gram gave 0·2830 carbonate, or 0·4641 gram nitrate of calcium. This corresponds to 25·36 per cent.

§ 213. The eutectic alloy of nitre with nitrate of strontium has a melting-point of 258°. Of this, 1·9490 gram gave 0·3498 gram carbonate, or 0·5031 gram nitrate. This corresponds to 25·81 per cent.

§ 214. The eutectic alloy of nitre with nitrate of barium melts at 278°·5. Of this, 2·6100 grams gave 0·5860 gram carbonate, or 0·7773 gram nitrate of barium. This corresponds with 29·53 per cent.

Eutectic alloys of :—

		Melting-point.
Nitre	74·64	251°
Nitrate of calcium . . .	25·36	
Nitre	74·19	258°
Nitrate of strontium . .	25·81	
Nitre	70·47	278°
Nitrate of barium	29·53	

In this group strontium holds its accustomed intermediate place between calcium and barium ; but, both in regard to the melting-point and to the composition of its eutectic alloy, it more closely resembles the former than the latter.

§ 215. *Nitre and Nitrate of Lead.*—The eutectic alloy formed by these salts is of great interest, not only because the lead element, like the chromate of potassium and the nitrates of barium and strontium, cannot be fused alone without decomposition, but because it, the alloy, has a remarkably low melting-point, and because either constituent in excess of its quantity in the eutectic alloy raises the melting-point in a manner easy to be followed. To the fused nitre the dry nitrate of lead is added, and on cooling one or other separates out in crystals easy to distinguish. More of the salt which is in fusion is added, until this is in its turn the one which separates on cooling. The same process having been repeated three or four times, the whole is allowed to lose heat as before. The temperature soon settles at 207° C., and thereupon the liquid begins to solidify as a beautiful white opaque porcelain-like mass, startlingly like the cryohydrates. The temperature may at first sink to 203° C.; and when in this condition of supersaturation, solidification is not to be induced by the introduction of dust of either of the nitrates, but begins when dust of the solid eutectic alloy is introduced. The temperature thereupon rises to 107°. This presumably proves that the alloy has a crystalline form of its own, different from those of its two constituents. Its composition was as follows, the lead being weighed as sulphate. The two specimens were from separate preparations, the only criterion of identity of composition being identity of melting-point.

(1) 2·8625 grams gave 1·2150 of sulphate of lead, or 1·3276 gram of nitrate of lead, or 46·38 per cent. of nitrate of lead.

(2) 2·3005 grams gave 0·9968 gram of sulphate of lead, or 1·0892 gram of nitrate of lead, or 47·34 per cent. Taking the mean, we have

Eutectic alloy of

		Melting-point.
Nitre	53·14	207°.
Nitrate of lead	46·86	

§ 216. *Nitre and Sulphate of Potassium.* — Anhydrous neutral sulphate of potassium dissolves in fused nitre, and separates out therefrom as the fused mass cools in the form of a fine powder. It is advantageous to allow the mass to lose heat very slowly. As soon as the porcelain-like eutectic alloy begins to be formed, the liquid is transferred into a fresh crucible, and the solidification is continued. An alloy is thus finally obtained of the constant melting-point of 300°.

2·6625 grams gave 0·0836 gram sulphate of barium, corresponding to 0·0627 gram sulphate of potassium, or 2·36 per cent.

Eutectic alloy of		Melting-point.
Nitre	97·64	300°.
Sulphate of potassium . .	2·36	

§ 217. Putting together the results of §§ 211–214, we have the following table, in which the alloys are, like the cryohydrates of table § 88, arranged according to the lowness of the melting-points.

Table XLIII.

Eutectic alloys with nitre.

Name of salt.	Temperature of fusion.	Per cent. of salt.	Per cent. of nitre.
Nitrate of lead	207°	46·86	53·14
Nitrate of calcium	251	25·36	74·64
Nitrate of strontium	258	25·81	74·19
Nitrate of barium	278	29·53	70·47
Chromate of potassium	295	3·76	96·24
Sulphate of potassium	300	2·36	97·64

Fused mixtures of nitre and the variable salt, which are richer in the salt than the eutectic alloy, give up that salt on losing heat; those which are poorer give up nitre, until in both cases the eutectic alloy is reached. The eutectic alloy is the exact analogue of the cryohydrate; and just as in the preceding memoir curves were drawn showing, on the one hand, the temperatures at which ice separates from salt-solutions of various strengths, weaker in salt than the cryohydrate, and, on the other, the temperature at which the salt, or occasionally a subcryohydrate, separates from such solutions as are stronger in salt than the cryohydrates, so, doubtless, the analogous curves could be drawn connecting the temperature at which solidification begins with the fused mixtures of salts (see § 223). And, again, as there are always two strengths of an aqueous solution, one stronger and the other weaker than the cryohydrate, which are both saturated at the same temperature below zero, one in respect to the salt and the other in respect to the ice, so with these fused mixtures there must be two such mixtures, from both of which a solid begins to separate at any given temperature between the melting-point of the most easily fused constituent and that of the eutectic alloy. § 223 is devoted to the tracing of this inquiry.

§ 218. The analogy is so perfect between the two groups of bodies (eutectic alloys and cryohydrates), that we may look with great confidence for homologous phenomena. The freezing mixture, or cryogen of my former memoirs, has its perfect counterpart amongst the salt-alloys, as follows :—

A layer of powdered nitrate of lead (46 parts by weight) is placed in the bottom of a wide test-tube. On this is laid a thin disk of mica, having a hole in the middle. A thermometer is fixed through the hole so that its bulb is half covered by the lead salt. Upon the mica, and so surrounding the top of the bulb, is piled some powdered nitre (54 parts). This tube is plunged into a bath of melted nitre, which is heated some few degrees above its melting-point, and until the thermometer registers about 250°. The thermometer is then used as a stirring-rod to mix the two salts. The mercury sinks to 207°, and remains pretty constant for a time at that temperature. The contents of the tube liquefy, and solid nitre is formed upon the outside of the tube. Now substitute ice for nitre, and perform the analogous experiment. The nitrate of lead and ice in the inner tube will form a freezing-mixture when stirred together, and this will cause ice to form on the outside, if the melted ice (water) in contact with it be not too warm.

§ 218A. Just as the eutectic metallic alloys had been nearly approached by Rudberg and others, so approximations to eutectic salt alloys have not been unknown. Thus M. Maumené (*Comptes Rendus*, 1883, xcviii. p. 1215) makes the very interesting statement that while neither nitrate of barium nor nitrate of lead can be fused *per se* without decomposition, they can both be so fused beneath a mass of nitrate of potassium or nitrate of sodium or a mixture of both. He states that an equivalent mixture of the nitrates of barium and sodium melts at about 370° ; and that when equal weights are taken, crystallization begins at 322°, and solidification takes place at 288°. Again, according to M. Maumené, equal weights of the nitrates of lead and sodium have a melting-point (*point fixe*) at 282° [we have seen that the eutectic alloy of these two fuses at 268° and contains 42·84 *per cent.* of nitrate of lead (see § 221)]. And again, M. Maumené, on taking equal weights of nitrate of sodium, nitrate of potassium, and nitrate of lead, finds the melting-point 259°. [I find (§ 215) an eutectic alloy melting at 186° and containing 43·34 nitrate of lead.] It appears that none of the proportions given by M. Maumené are those of the eutectic alloys, and that accordingly the temperatures of solidification which he gives cannot be constant.

§ 219. *Eutectic Salt Alloys of Nitrate of Sodium.*—Nitrate of sodium fuses at 305°, and we might perhaps expect that its eutectic alloys would have lower fusing-points than the corresponding nitre alloys. The following experiments show that this is by no means the case.

§ 220. *Nitrate of Sodium with Nitre.*—Obtained by the method above described, the eutectic alloy of these two salts has the fusing-point of 215° C. Of this alloy 3·8885 grams were converted into neutral sulphates, having the joint weight 3·3135. This implies 2·5093 grams nitre and 1·3792 gram nitrate of sodium; or

	Per cent.	Melting-point.
Nitrate of sodium . . .	32·90	215°.
Nitrate of potassium . .	67·10	

For the specific gravity of this alloy, see § 228.

§ 221. *Nitrate of Sodium with Nitrate of Lead.*—This eutectic salt alloy has a melting-point of 268°. A weight of 3·3040 grams gave 1·2955 grams sulphate of lead, which corresponds to 1·4156 gram nitrate of lead.

	Per cent.	Melting-point.
Nitrate of sodium . . .	57·16	268°.
Nitrate of lead . . .	42·84	

§ 222. *A Tri-eutectic Alloy.*—Let us consider for a moment the alloy in § 219 to be a single salt, and find the eutectic alloy between this and nitrate of lead. The lowest melting-point is found to be 186°; and the composition of the alloy, derived from the result that 2·9280 grams gave 1·1613 gram sulphate of lead or 1·2690 gram nitrate of lead, is as follows:—

	Per cent.	Melting-point.
Nitrate of potassium . .	38·02	186°.
Nitrate of sodium . .	18·64	
Nitrate of lead . . .	43·34	

This of course implies that the above is the eutectic alloy of these three salts. The eutexia of salt alloys of more than two salts is a very wide question upon which I can only here touch.

§ 223. The following experiment completes the analogy pointed out in § 218. Mixtures of nitre and nitrate of lead, both in the form of powder, were made in different ratios from 95 nitre and 5 of nitrate of lead, 90 of nitre and 10 of nitrate of lead, and so on; these were put into test-tubes and heated in an oil-bath, which was kept continually stirred. The mixture was completely melted, and the temperature at which solidification began was observed. The observations, being repeated many times, gave the following results:—

Temperatures at which solidification begins in melted alloys of nitre with nitrate of lead of various strengths.

TABLE XLIV.

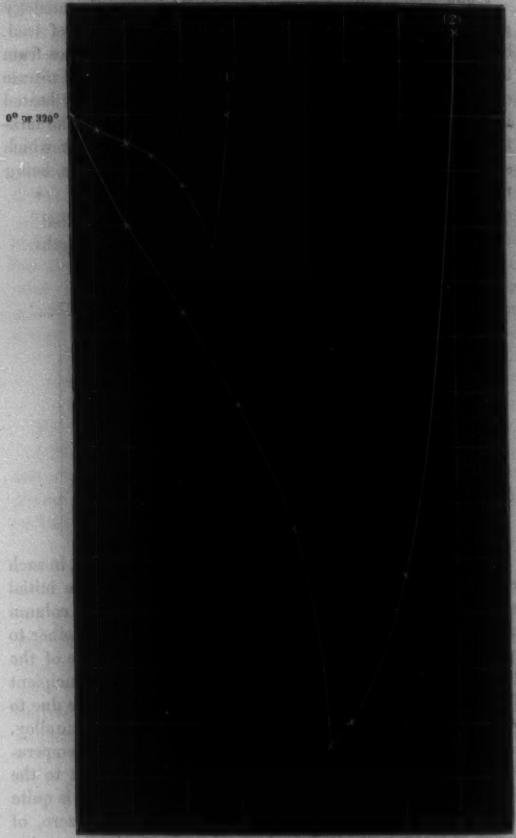
Nitre per cent.	Nitrate of lead per cent.	Temperature of beginning of solidification.	Nature of body separating.
100	0	320°	Nitre.
90	10	300	"
80	20	285	"
70	30	268	"
60	40	246	"
53·14	46·86	207	Eutectic alloy.
50	50	210	Nitrate of lead.
40	60	238	"
30	70	335 (?)	"

It is of course necessary to heat the mixed powders, in each case, beyond the temperature which proves to be the initial solidifying point of the mixed mass. On heating the column of powder it is noticed first to shrink and cake together to about a quarter of its former volume, reminding one of the baking of clays. Indeed all phenomena of so-called incipient fusion of compound bodies (the pasty state) may be due to what takes place here, namely the formation of an eutectic alloy.

The decomposition of both terms of this alloy, at temperatures not very much higher than 320°, puts a limit to the tracing of this curve further, but its general aspect is quite like that of the salt-solution (water) curves below zero, of which so many examples have been given in previous memoirs.

Mixtures consisting of 20 per cent. nitre and 80 per cent.

nitrate of lead, and even 10 per cent. nitre and 90 per cent. nitrate of lead, fuse together into clear liquids without decom-



position, but I have not determined the melting-points. At a higher temperature the red peroxide of nitrogen is evolved, but I do not know whether it is or is not accompanied by oxygen.

In the figure curve (1) shows the solidification-temperatures of mixtures of nitrate of lead and fused ice (§ 152), and curve (2) shows the solidification-temperatures of mixtures of nitrate of lead and fused nitre. The abscissæ are on the same scale (1 millim. to 1 per cent. of lead salt). The ordinates are in (2) 1 millim. to 1° C.; in curve (1) 1 millim. to 0°·1. The curve (2) is fetched down so that the two have a common origin.

§ 224. One of the widest generalizations with regard to the behaviour of compound bodies towards one another is that which assumes, in the case of two salts, that the bases are shared in the first place by the acids, and that the result which often ensues, that one base and one acid are ultimately found in union to the exclusion of all others, is due to the successive withdrawal of such a combination when formed, either by its insolubility or volatility. Accordingly we must not be surprised that when the conditions of insolubility are varied, the final selection may be wholly changed. The salt alloy described in § 215, namely the eutectic alloy of nitre and nitrate of lead, when mixed with the eutectic alloy of nitre and sulphate of potash, § 216, and heated, forms a perfectly transparent liquid. Sulphate of lead, which is so insoluble in water, is soluble in fused nitre (see § 225); and a mixture may be got identical with that got on heating nitrate of lead with sulphate of potassium in the presence of nitrate of potassium. There is in both cases equilibrium between the bases and acids. When sulphate of lead is dissolved in fused nitre, it is to be noticed that, at a considerably increased temperature, the red oxide of nitrogen is given off, as when nitrate of lead is heated by itself. Both nitre and sulphate of lead, when heated by themselves, require a much higher temperature for their decomposition; this seems to show the existence of nitrate of lead in the fused mixture. The liquidness of the fused alloy does not show that no sulphate of lead is present: a certain amount of lead is no doubt in union with sulphuric acid, but is soluble in nitre as other salts are soluble in water.

§ 225. *Nitre and Sulphate of Lead.*—On adding pure dry sulphate of lead to fused nitre, solution ensues the more abundantly the hotter the liquid. The amount of sulphate of lead dissolved is, however, small, and the fusing-point is only lowered about 5°, standing now at about 315°. At temperatures above its melting-point, it would be unjustifiable to call such a liquid an alloy, because its composition, in all probability, depends upon its temperature in as far as that composition is referred to the distribution of acids and bases. As it cools it gives up sulphate of lead in little crystals which sink. At the temperature of 315° general solidification begins, and is completed.

Of this alloy 4·2725 grams were treated with water and a little alcohol, and the insoluble sulphate of lead was found to weigh 0·1968 gram, corresponding to 4·61 per cent.

Sulphate of lead requires for fusion *per se* a bright red, almost white heat. But it is thus found to dissolve in hot fused nitre, and it separates as such on cooling the fused liquid. For the geological value of this fact see § 230.

§ 226. *Sulphate of Calcium* behaves in a similar manner. Highly refractory by itself, it dissolves in fused nitre. The cooling mixture, after shedding the excess of sulphate above that required for the eutectic alloy, solidifies at a constant temperature of about 315°. The lime, separated as oxalate and weighed as carbonate, showed a percentage of sulphate of 0·93. For 3·4832 grams of alloy gave 0·0238 gram of carbonate, or 0·03237 gram of sulphate.

§ 227. *Nitre and Sulphate of Barium.*—Even the sulphate of barium, which is typical of aqueous insolubility, dissolves in fused nitre, depressing the solidifying point, however, almost inappreciably. A little separates on cooling, and 8·54 grams of the eutectic alloy, when boiled with water, gave 0·0852 gram of the insoluble sulphate, or 0·98 per cent. It may be noticed in passing that, as is well known to analysts, sulphate of barium is soluble to an appreciable extent in another fused nitrate, namely nitrate of hydrogen.

§ 228. *Specific Gravity of the Eutectic Alloy of Nitrate of Potassium and Nitrate of Sodium.*

Slabs of nitre, nitrate of sodium, and the eutectic alloy of the two were cast upon a surface of cold metal, the liquids themselves being when poured only a few degrees above their melting-points. Their specific gravities were found by weighing them in oil of turpentine of ascertained specific gravity. I found the

Specific gravity of nitre	2·2028
„ „ nitrate of sodium	2·0469
„ „ the eutectic alloy	2·1328

If the two were to mix without either gain or loss of volume in the proportion found in § 220, namely 32·9 of nitrate of sodium and 67·1 of nitrate of potassium, the specific gravity of the alloy would be 2·149. The density found shows that there has been an expansion on the two associating themselves together to form the alloy. And this expansion is presumably in near connexion with the lowering of the melting-point.

§ 229. The generalization of Berthollet is only one aspect of the question of distribution. When a compound body $a\,x$ and another compound body $b\,y$ being brought together in watery solution give rise to an insoluble body $a\,y$ and a soluble one $b\,x$, we have no more right to say that the change is brought about in virtue of the insolubility of $a\,y$ than that it is due to the solubility of $b\,x$. Strictly speaking, it is due to the difference in solubility of the two. For the solubility of the one is as much concerned with the separation of the two new compounds as in the insolubility of the other. It is on this account that eutexia, without water, and as it exists in the case of two fused metals or anhydrous salts, may and must have a determining influence on the arrangement in ratio or kind of the constituents.

§ 230. *Geological and Mineralogical Significance of Eutexia.*—How the temperature of liquefaction of rocks may be lowered by the introduction of even small quantities of water will be discussed in my next memoir. It has been very diligently considered by Daubrée. Let us briefly examine the question of the interaction of rocks and their constituents, without, of necessity, the intervention of water.

In reviewing the analyses of Felspathic minerals, most of which, unless weathered after solidification, appear to be essentially anhydrous, we find them to be silicates of potassium and aluminum, in which, to use the common expression, the potassium is partly replaced by sodium, calcium, magnesium, and manganese, the aluminum by iron. That water is not essential to the formation of this kind of mineral, is proved by the occurrence of it in copper and iron furnaces. Mica, on the other hand, appears always to contain water, sometimes as much as three or four per cent., with a lesser percentage of silica than felspar; it contains generally a far larger proportion of aluminum and of iron; the abundance of the latter element may indeed be considered, together with its deficiency in silica, as its distinguishing characteristic, chemically speaking, from orthoclase.

Silica—the great earth-acid, a title which it shares with carbonic acid, whose other realm is the air, and to some extent with hydrochloric acid, whose proper region is the sea—appears both in the anhydrous form and with as much as eleven per cent. of water. By its union with alumina it gives rise to clay, slate, and the minerals staurolite, andalusite, kyanite; with lime to Wollastonite; with magnesia (and iron) to bronzite; with lime and magnesia (and iron) to augite and diallage; with magnesia and iron (and lime) to hypersthene and olivine; with magnesia, lime, and iron to hornblende; with iron to Fayalite, and so on.

If, now, we adopt the often-asserted theory that variations in minerals belonging to the same class are brought about by the exchange of more or less of one base by another, the analyses land us in a difficulty, which seems insuperable. Let us suppose, for instance, that we have pure Wollastonite, consisting of

Silica	51·73,
Lime	48·27.

Replacing part of the lime by magnesia and iron, say 23·51 by 18·55 magnesia and 0·99 protoxide of iron, the silica rises to 55·15, and gives us an excellent example of augite (neglecting the manganese and alumina of that body).

	V. Bonsdorff.
Silica	54·83
Lime	24·76
Magnesia	18·55
Protoxide of iron	0·99
Protoxide of manganese	0·32
Alumina	0·28

But next let us examine hornblende, an analysis of which by V. Bonsdorff is given.

Silica	60·10
Magnesia	24·31
Lime	12·73
Protoxide of iron	1·00
Protoxide of manganese	0·47
Alumina	0·42
Hydrofluoric acid	·83
Water	·15
	100·01

These bases, neglecting the water and hydrofluoric acid, require together 51·83 of silicic acid, instead of 60. No process of exchange of one base for another can make hornblende out of Wollastonite. It is essentially acid, unless in those varieties of amphibole which contain a considerable proportion of alumina; these, indeed, may be basic, acid, or neutral, according as the alumina is considered as a base saturating the silica, or an acid saturating lime or magnesia, or partly in the one predicament and partly in the other. As Wollastonite occurs along with amphibole and augite, there does not appear sufficient ground for this essential difference on the replacement theory.

I submit that, according to analogy, we should regard compound rocks and minerals, other than sedimentary rocks, as representing various kinds of eutectic alloys. We may for the sake of argument start from some known definite rock which is a true chemical compound, such as orthoclase, and trace the probable reactions between this and other rocks; or we may take a rock, like granite or syenite, of indefinite composition, and examine the probable assortment of its constituents on cooling. Starting with the melted mass, my experiments with salts have, I maintain, established that the clear molten granite will in cooling throw off as solids atomically definite salts, the last alloy to remain liquid being the eutectic alloy, which is constant only in composition in the sense in which such a body is so. It would follow therefore that the micas are the eutectic alloys of the proximate elements, or salts of the melted granite. Quartz and felspar being both molecularly constituted, undergo solidification before mica. On account of the enormous effect which even a little water has in reducing the melting-point [*] and because silica is soluble in water, it is probable that the order of solidification is first felspar, and then quartz, and lastly mica. Quartz is thus speaking *en gros* pseudomorphic to felspar, and mica to both; all three are sometimes in this mass-sense pseudomorphic to slate, and mica is especially so. If fused nitre be saturated with nitrate of lead and sulphate of potash, and gradually cooled, sulphate of lead first separates, then sulphate of potash with sulphate of lead, then the eutectic alloy of all three. The sulphate of lead represents the felspar, the sulphate of potash with sulphate of lead represents the quartz, and the eutectic alloy represents the mica (see also § 38, Phys. Soc. Proc. 1874). Tourmaline and hornblende are probably both eutectic, whilst olivine is probably not.

§ 231. As to the great rock-masses themselves, if we assume that the earth is a drop of fused rock alloy with a solid crust, and that its history had been one of gradual undisturbed and symmetrical cooling, it is clear that, apart from sedimentary formations, the oldest solid rocks are those formed nearest the surface. But the disturbing causes are manifold: the earth-crust is under stress on account of the loss of volume on cooling. This strain is unequally distributed, on account of the want of sphericity of the earth's form, and on account of the centrifugal pressure towards the equator. Extra-terrestrial influences, such as the conjunction and apposition of the sun and moon and the variation in solar radiation, are asymmetrical, so that the earth's crust heaves and cracks and allows the eutectic melted alloy to break through, and as an intrusive mass metamorphose and overlie the older formations. Once rendered asymmetrical, the geographical features give rise to climates and weathers, and determine the formation of the sedimentary strata.

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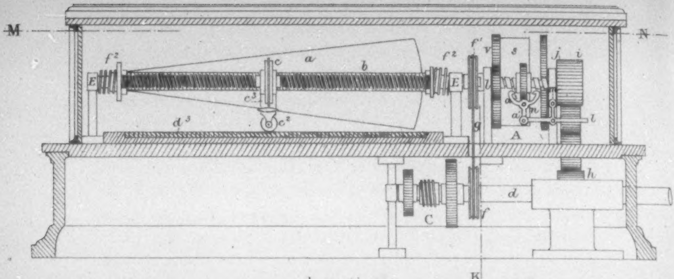
[*] See Daubrée, *Géologie expérimentale*. Also my next memoir, §§ 339-345.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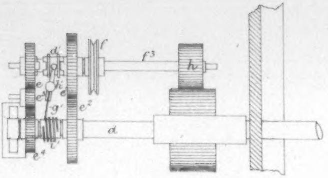
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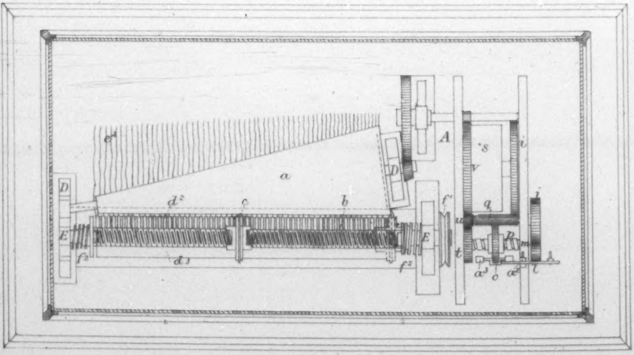
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Mintern Bros. lith.

XII. *On a "Speed Indicator" for Ships' Propellors.* *By* Sir Archibald Campbell of Blythswood *and* W. T. Goolden*.

[Plate IX.]

In February of last year, when visiting one of H.M. Dockyards, it was pointed out to us that a very urgent need was felt of some means of indicating with certainty the speed of naval engines, especially in ships carrying twin-screws, where the engines are not only distinct, but separated from each other by iron bulk-heads which prevent any communication between the two engine-rooms. The authorities intimated also that it was desired that several indications should be made simultaneously in various parts of the ship, and that the apparatus should be as far as possible automatic, and require no trouble or attention.

There are at present one or two instruments in existence for this purpose, but their indications are found to be untrustworthy when at sea; and we were warned that no instrument in which the force of gravitation played a part would be likely to receive any attention at the Admiralty. This consideration excludes the use of ball-governors or of any device depending on the weight of a fluid column; and led us to consider whether the desired conditions could not be fulfilled by a purely mechanical arrangement founded on the ordinary equation involving angular velocity,

$$v = r\omega.$$

It was at first difficult to see how this principle could be applied to a direct measure of ω, as no simple means are known whereby the variation in the velocity v of a point moving in a straight or curved path can be continuously measured. But it was soon apparent that the variable angular velocity ω of a body A can be compared with the constant angular velocity ω' of another body B, if a point on B at a distance r' from its axis of rotation has the same linear velocity as a point on the circumference of A. We then get

$$\omega = \frac{\omega'}{r} r',$$

in which $\frac{\omega'}{r}$ is constant, and thus ω varies as r'.

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* Read May 24, 1884.

The condition is evidently satisfied by a disk pressing on the surface of a cone revolving at a uniform speed ; for the linear velocity of the point in the perimeter of the disk which is in contact with the cone, being identical with that of the corresponding point of the cone, will be proportional to the radius of the corresponding circular section of the cone, and consequently to the distance of the point of contact from the apex of the cone. If, further, the disk forms the nut of a screw rotating in the opposite direction to the cone, and the axis of the screw is placed parallel to the side of the cone, it is obvious that the nut and screw must have the same angular velocity for the nut to be at rest on the screw ; and the disk will therefore take up a different position on the screw as the velocity of the latter changes in value.

In the "Blythswood Speed Indicator" the screw is driven by the engine or shaft whose speed is to be indicated, while the cone has a constant speed communicated to it by clockwork. A scale placed under the screw shows the speed of the nut and screw when the nut is at rest ; and by a series of electric contact-pieces attached to a cable, the indications can be transferred to dials placed at any distance from the machine.

When the engines reverse, a clutch keeps the screw revolving always in the same direction, and at the same time pulls over a commutator placed in the electric circuit, so that the dials show not only the speed, but also the direction of motion, ahead or astern.

The clock is wound by the engine, and stops when the machinery is at rest ; and having a carefully balanced friction-governor, it is independent of gravity, and therefore keeps its time under all conditions of wind and weather.

We propose to add to the instrument a drum carrying prepared paper, upon which as it revolves a pencil will continuously trace the position of the nut, and thus keep a record of the performance of the engine for future reference.

The same principle can evidently be applied to a comparison of the speeds of two engines or rotating shafts, where both are variable, if one drives the cone and the other the screw, for $\frac{\omega}{\omega'} = \frac{r'}{r}$, in which r is constant.

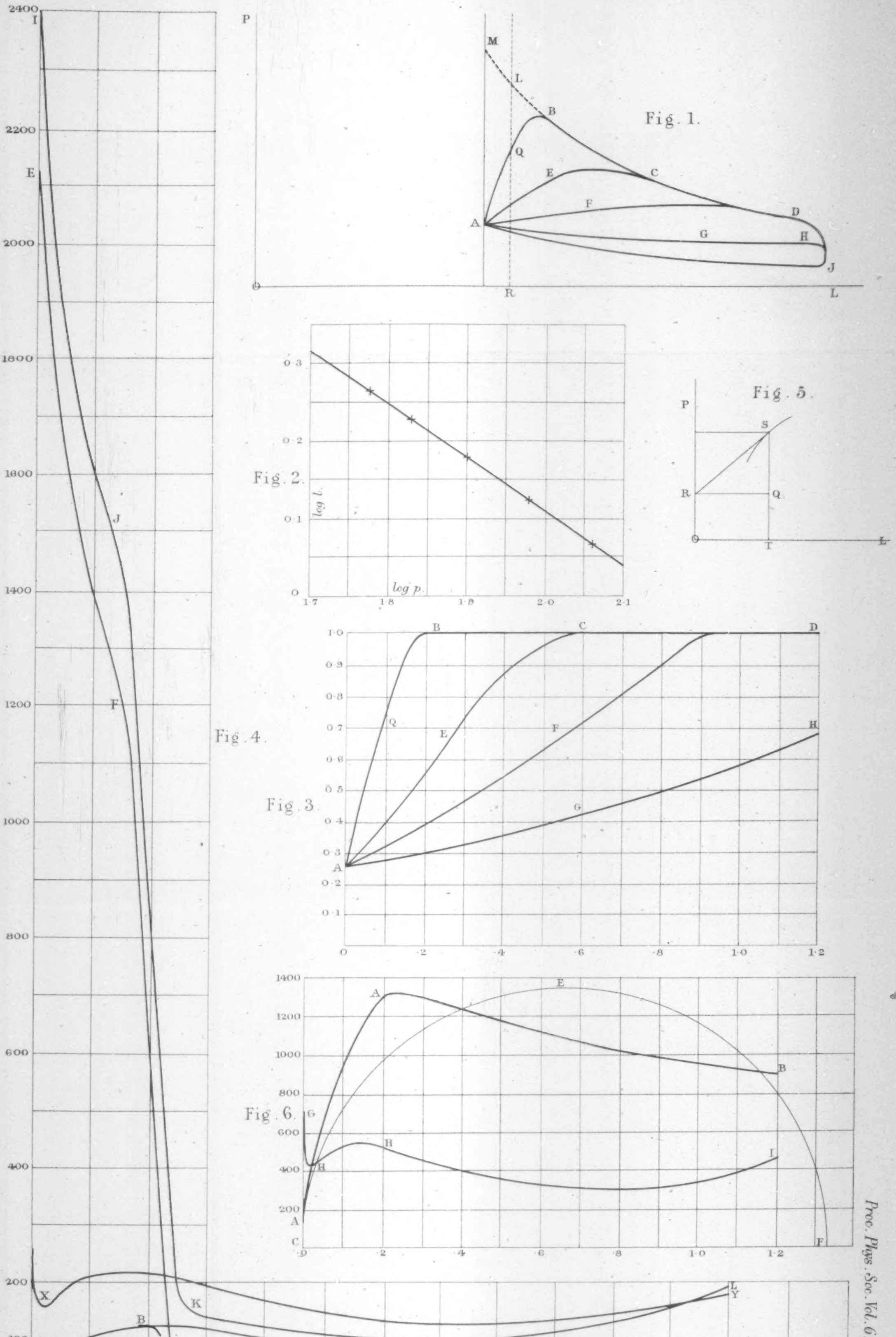

Fig. 1.

Fig. 2.

Fig. 5.

Fig. 3.

Fig. 4.

Fig. 6.

Mintern Bros. lith.

We desire in conclusion to express the obligation we are under to Mr. Hilger for the admirable skill and patient intelligence with which he has successfully carried out our idea.

XIII. *The Gas-Engine Indicator-Diagram.* *By* Professors W. E. AYRTON, *F.R.S., and* JOHN PERRY, *M.E.*[*]

[Plate X.]

THE members of this Society are probably aware that gas-engines are now largely in use, and that their use is still extending rapidly. There can be no doubt that gas-engines would be largely used, even if they were wasteful of fuel, on account of their being always ready to start or stop, and their requiring so little attention; but it is gradually becoming clearer that even small specimens of this kind of engine, whose history is merely beginning, are in actual fact less wasteful of fuel than the largest and most carefully constructed steam-engines. It is, for example, a demonstrated fact that, with a Dowson's generator not larger than the boiler used in the corresponding steam-engine, an Otto engine uses only 1·1 lb. of coal per indicated horse-power per hour. It is therefore not unreasonable to suppose that gas-engines will soon be employed even in the propulsion of ships.

The rapid growth of this new application of science renders it necessary that help should be given to practical men to enable them to use such observations as they are constantly making. This paper is intended to teach such men a *method* of obtaining information from the indicator-diagram of a gas-engine.

2. *The Action in the Otto Gas-Engine.*—This large model which we exhibit has been constructed in the workshop of the Finsbury College, to enable students to follow the motions of different parts of the gas-engine. It will be seen that when the piston is at the end of its stroke, only what we call the clearance-space behind it is filled with fluid. This fluid is a mixture of carbonic acid, water-vapour, and nitrogen, whose

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[*] Read April 26, 1884.

temperature is about 410° C.*, if there was an immediately previous explosion. The temperature of the clearance-space fluid may be anything between 410° C. and the temperature of the atmosphere, depending on how recently an explosion has taken place. As the piston moves forward it draws into the space a mixture of gas and air. At the end of the forward stroke the pressure of the mixed fluid is nearly that of the atmosphere; in the back stroke the fluid is compressed. At the beginning of the next forward stroke the fluid is ignited, and rapid development of heat results, causing great increase in pressure, the pressure gradually diminishing until, just before the end of the forward stroke, the fluid is allowed to escape. In the next back stroke the piston drives the fluid out of the cylinder with the exception of what remains in the clearance, and thus completes a cycle of operations. In fig. 1 (Pl. X.) indicator-diagrams show the nature of the alterations in pressure and volume going on during the compression and working parts of the cycle; distances measured from O L representing pressure in pounds per square inch from vacuum, and distances measured from O P representing volume of the fluid, the unit of volume being the volume described by the piston moving through one foot of the length of the cylinder.

Four different diagrams are given whose compression parts practically coincide, the differences in their ignition parts being due to differences in the amounts of gas supplied. We have not thought it necessary to give a complete diagram in which the dismission and suction parts of the cycle should be represented.

The shape of the diagram is materially modified by the recentness of the last explosion, as this affects the temperature of the fluid before compression, and so modifies the actual amount of the mixture of gas and air entering the cylinder. To a less degree the shape of the diagram is affected in the discharge part of the cycle by the recentness of an explosion, as a recent explosion will have given the exhaust passages a higher temperature.

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* In our own observations at Finsbury we have not used any specially contrived apparatus, as our investigations were really for the purpose of enabling students to illustrate for themselves a course of lectures delivered by one of us on the Gas-engine. Hence we have taken the temperature of 410° C. as the exhaust temperature, instead of 300° C. given by our own measurements with the Siemens pyrometer. A correction of this temperature would perhaps lessen the number 1·57 W and increase 0·37 W, given in § 9.

3. *The Nature of the Working Fluid.*—For the purpose of showing the nature of the working fluid we have constructed Table I. It will be seen from this that a mixture of 6·760 cubic feet of air and coal-gas becomes, after complete combustion, 6·4977 cubic feet of carbonic acid, water-vapour, and nitrogen, reduced to the same pressure and temperature without condensation of the water-vapour. Now as there is always an excess of air, and as the mixture before combustion has added to it nearly six cubic feet of the products of previous combustions, we have something like 13·3 cubic feet before combustion becoming 13·0377 cubic feet after combustion, at equivalent pressures and temperatures. The contraction is only about 2 per cent. We therefore conclude that we may regard the fluid in a gas-engine as a fluid which, however it may receive heat, obeys approximately the characteristic law,

$$\frac{pv}{T} \text{ constant}$$

(where p is pressure, v volume, and T the absolute temperature), in so far as mechanical actions are concerned. That is, we may speak of it as a perfect gas, which receives heat from without, neglecting the fact that it is its own molecular energy which appears as heat. It is also approximately true that the ratio of the specific heats of the fluid is unchanged by combustion taking place.

In Table II. we give a similar comparison for Dowson gas :—

2·1325 cubic feet of combustible mixture become 1·9143 cubic feet ;

or, taking into account the clearance-space and its products of past combustions, we have, say,

4 cubic feet becoming 3·7818 cubic feet ;

or contracting by nearly 5½ per cent. of its volume.

In Tables III. and IV. we calculate the specific heat of a mixture of 1 cubic foot of coal-gas, 5·76 cubic feet of air, and 4·5 cubic feet of products of a previous combustion, before and after combustion takes place. The Centigrade scale of temperature is employed.

In Tables V. and VI. similar calculations are made for the usual mixture of Dowson gas with air and products of previous combustion.

TABLE I.—Coal-Gas.

	Hydrogen, H_2.	Carbonic oxide, CO.	Marsh-gas, CH_4.	Olefiant gas, C_2H_4.	Tetrylene, C_4H_8.	Nitrogen, N.	Carbonic acid, CO_2.	Water-vapour. H_2O.	Total.
Cubic feet in one cubic foot of gas	0·4600	0·0750	0·3950	0·0253	0·0127	0·0050	0	0·0200	
Heat evolved per cubic foot of each	191·12	190·02	592·6	932	1702	0	0	0	
Heat evolved by given amount of each	87·92	14·25	234·1	23·58	21·61	0	0	0	381·46 or 530,230 foot pounds.
Oxygen required by one cubic foot of each	0·5	0·5	2	3	6	0	0	0	
Product of combustion per cubic foot of each...	1·0	1·0	3	4	8	0	0	0	
Oxygen required by given amount of each	0·2300	0·0375	0·790	0·0759	0·0762	0	0	0	1·2096 cub. ft. of oxygen per cub. [ft. of gas. or 5·760 ,, ,, air ,, ,, ,,
Volume of product of combustion	0·460	0·075	1·1850	0·1012	0·1016	0·005	0	0·020	1·9478+4·5499 of nitrogen, or 6·4977.

TABLE II.—Dowson Gas.

	Hydrogen, H_2.	Carbonic oxide, CO.	Marsh-gas, CH_4.	Olefiant gas, C_2H_4.	Tetrylene, C_4H_8.	Noncombustible.	Total.
Cubic feet in one cubic foot of gas	0·1873	0·2507	0·0031	0·0020	0·0011	0·5555	
Heat evolved per cubic foot of each...............	191·12	190·02	592·6	932·05	1702	0	
Heat evolved by given amount of each	35·79	47·63	1·837	1·864	1·872	0	88·99, or 123696·1 foot-pounds.
Oxygen required by given amount of each	0·0936	0·1254	0·0062	0·0060	0·0066	0	0·2378 cub. ft. of oxygen per cub. ft. of gas, or 1·1325 ,, ,, air ,, ,, ,,
Volume of product of combustion	0·1873	0·2507	0·0093	0·0080	0·0088	0	·4641+·4898 of N in gas +·0657 of CO_2 in gas + ·8947 of N in air introduced =1·9143.

TABLE III.—Coal-Gas before Combustion.

Constituent.	Amount in fluid.	Specific heat at constant pressure per unit volume.	Specific heat at constant volume per unit volume.		
	Cubic feet. q.	C_p.	C_v.	qC_p.	qC_v.
Hydrogen	0·46	·2359	·99 × ·168	·1085	·4554 × ·168
Carbon monoxide	0·075	·237	1 ,,	·0178	·0750 ,,
Marsh-gas	0·3950	·3277	1·54 ,,	·1294	·6082 ,,
Olefiant gas	0·0380	·4106	2·03 ,,	·0156	·0771 ,,
Nitrogen	0·0050	·237	1 ,,	·0012	·0050 ,,
Water-vapour ...	0·0200	·2984	1·36 ,,	·0060	·0272 ,,
Air	5·76	·2374	1 ,,	1·3680	5·760 ,,
Products	4·5	·2581	1·124 ,,	1·1614	5·058 ,,
Total	11·253	......	......	2·8079	12·066 × ·168 or 2·027
Or $C_p=0·2496$, $C_v=0·1802$. Ratio .... 1·385.					

TABLE IV.—Coal-Gas after Combustion.

	Cubic feet. q.	C_p.	C_v.	qC_p.	qC_v.
Water-vapour ...	1·3714	·2984	1·36 × ·168	·4092	1·865 × ·168
Carbon dioxide ...	0·5714	·3307	1·55 ,,	·1889	·8855 ,,
Nitrogen	4·5554	·2370	1 ,,	1·0790	4·5554 ,,
Total	......	......	......	1·6771	7·3059 × ·168 or 1·227
Or $C_p=0·2581$, $C_v=0·1889$. Ratio ...... 1·367.					

TABLE V.—Dowson Gas before Combustion.

	Cubic feet. q.	C_p.	C_v.	qC_p.	qC_v.
Hydrogen	·1873	·2359	·99 × ·168	·0442	·1854 × ·168
Carbon monoxide.	·2507	·237	1 ,,	·0594	·2507 ,,
Marsh-gas	·0031	·3277	1·54 ,,	·0010	·0048 ,,
Olefiant gas	·0031	·4106	2·03 ,,	·0013	·0063 ,,
Nitrogen	·4898	·237	1 ,,	·1161	·4898 ,,
Carbon dioxide ...	·0657	·3307	1·55 ,,	·0217	·1018 ,
Air	1·1325	·2374	1 ,,	·2689	1·1325 ,,
Products	2	·2594	1·1323 ,,	·5188	2·2646 ,,
Total	4·1322	......	......	1·0314	4·4359 × ·168
				·2496	1·0735 × ·168 or ·1803
Ratio .... 1·385.					

TABLE VI.—Dowson Gas after Combustion.

	q.	C_p.	C_v.	qC_p.	qC_v.
Water-vapour ...	0·2019	·2984	1·36 × ·168	·0602	·2746 × ·168
Carbon dioxide ...	0·3279	·3307	1·55 „	·1084	·5083 „
Nitrogen	1·3845	·2370	1 „	·3281	1·3845 „
				·4967	2·1674 „
Total	1·9143	......	......	·2594	1·1323 × ·168 or ·1902
Ratio .... 1·3637.					

The specific heats here given are those of the constituents in the cold state. Seeing, however, that there is no great change due to combustion, we may for many practical purposes assume that the specific heats remain the same at all temperatures. We have less right when using Dowson gas than when using coal-gas to make our assumption, which is that the fluid in the gas-engine, from the beginning of its compression until it is allowed to escape, behaves like a perfect gas, receiving heat from an outside source.

4. *Study of the Shapes of the Compression and Expansion parts of the Diagram.*—The first problem which comes before us is the determination of the shape of the indicator-diagram. For the sake of illustration we mean to investigate the series of diagrams shown in fig. 1, diagrams taken from a 6-horse power Otto engine at the Finsbury College, using coal-gas. It will be observed that, although the ignition parts of the various diagrams differ greatly, on account of differences *in the amounts of gas supplied*, the curves agree in their compression and expansion parts. It is known to us that the clearance-space is 0·4 of the whole space occupied by fluid when the piston is fully at the end of its stroke. If λ is the distance in feet passed through by the piston from the end of its stroke, the stroke being $1\frac{1}{3}$ foot, the clearance is 0·889 foot, and $\lambda + 0{\cdot}889$, or l feet expresses the volume of the fluid at any instant. Measurements of l and p were made on the expansion-curves of the indicator-diagrams, and tabulated with $\log l$ and $\log p$.

We are making arrangements for measuring the clearance-space with accuracy. The above assumption is made from statements of the manufacturers, and may possibly be slightly in error. Such an error is of but small importance to us at present, as our object is to teach a method of study rather than to give results of the use of the method.

If we assume the law of the expansion-curve to be

$$pl^m \text{ constant,}$$

we have $\log p + m \log l = k$; so that when we plot $\log p$ and $\log l$ on squared paper as coordinates of points, these points ought to lie in a straight line if our assumption is correct. Fig. 2 (Pl. X.) shows how the points determined by the measured numbers lie; and it is obvious that they lie very nearly in a straight line. Taking the straight line which lies most evenly among them, we find that it is defined by

$$\log l = 0{\cdot}313, \quad \text{when } \log p = 1{\cdot}7,$$

$$\log l = 0{\cdot}0425, \text{ when } \log p = 2{\cdot}1.$$

Hence

$$1{\cdot}7 + 0{\cdot}313\, m = k,$$

$$2{\cdot}1 + 0{\cdot}0425\, m = k.$$

Hence

$$m = 1{\cdot}479 \text{ and } k = 2{\cdot}1629.$$

Now

$$\log 145{\cdot}5 = 2{\cdot}1629.$$

Hence the law of expansion is

$$pl^{1{\cdot}479} = 145{\cdot}5. \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

In the same way we find that the law of the compression-curve is

$$pl^{1{\cdot}304} = 39{\cdot}36. \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

It is obvious that the expansion-curve (1) is steeper than the adiabatic, if we assume that the ratio of specific heats of the fluid is 1·37, as the equation of the adiabatic curve is

$$pl^{1{\cdot}37} = \text{constant.}$$

Again, the compression-curve (2) has less slope than the adiabatic.

5. *Influence of Vibrations of the Indicator-spring.*—We wish to point out that it is exceedingly necessary, in obtaining the law of expansion, to take many points in the curve, and, either

by using the algebraic method or by the use of squared paper, to determine the most probable values of the constants. Engineers are constantly in the habit of determining these constants from measurements of the coordinates of two points only in the curve, forgetting that the position of either point may be much influenced by the vibrations of the spring of the indicator. The sinuous shape of the expansion-curve is specially noticeable in the early part of the expansion-curves of gas-engine diagrams.

It is further to be remarked that the vibration of the indicator-spring is very visible in the expansion part, because we have every reason to believe that the expansion part ought to have no sinuosities ; but it is our belief that this vibration has its effect on the explosion part of the curve as well, and that it is of the utmost importance to find some means of eliminating the effects produced by these vibrations of the indicator-spring.

In our communication to the Journal of the Society of Telegraph Engineers, p. 391, vol. v. (1876), we showed how to eliminate such vibrations in any case where the effect to be measured followed a regular law of increase or diminution, as in the case of the expansion part of this indicator-diagram. We have not yet sufficient information to enable us to employ this method on the explosion part.

The rule which we arrived at is as follows:—Draw two curves, A and B, through the highest and lowest points of the wavy curve which represents the actual observations : draw ordinates : the points of bisection of the parts of the ordinates intercepted between A and B lie on the correct curve.

6. *Empirical Formula for the whole Diagram.*—Now, inasmuch as the compression and expansion parts of all the curves follow the same laws, it would seem to be important to obtain one general formula for all the diagrams with one or more variable parameters. We have found that when we produce the expansion-curve (using formula 1), as shown at B M (fig. 1), and when we divide the pressure Q R at any part of the stroke by the corresponding ordinate L R of the expansion-curve, doing this for many parts of the stroke, we get the ordinate of an interesting curve. We have done this for the four diagrams of fig. 1, and obtain the four curves A Q B D, A E C D,

A F D, A G H of fig. 3. From a study of these curves, which are nearly formed of straight lines, it will be found that the ignition and expansion parts of any diagram satisfy approximately the law

$$p=145\cdot5\,l^{-1\cdot479}\{\kappa'+n\lambda-\sqrt{(\kappa-n\lambda)^2+s}\}. \quad . \quad . \quad (3)$$

The smaller the value of s the more nearly do the curves of fig. 3 approach straight lines. In our present case $\lambda=l-0\cdot889$, $\kappa'=0\cdot6343$, $\kappa=0\cdot3637$; $s=0\cdot0087$, and n has different values for the four diagrams. These constants are evidently easily calculated from any diagrams. For the curve shown as A B C D in fig. 1 (Pl. X.) the value of n is 2·2876. Using this value and calculating p for the following values of l, we have

TABLE VII.

λ.	l.	Observed. p.	Calculated. p.	Expansion-curve calculated. p.
0	·889	45	45	173
·061	·950	86	83	157
·111	1·000	108	108	146
·170	1·059	123	124	134
·211	1·100	126	125	126
·311	1·200	111	111	111
·511	1·400	88	88	89
·711	1·600	72	73	73
·911	1·800	60	61	61
1·111	2·000	52	52	52

The differences between the observed and calculated values of p are within the limits of errors of observation therefore. It may be that there is a discontinuity in the ignition-curve at $\lambda=\cdot061$ for a mixture of gas and air; but no discontinuity shows itself in the indicator-diagram in a sufficiently marked manner to be distinguished from vibrations due to the spring of the indicator.

As we have already stated, the recentness of the last explosion affects the temperature of the mixture of gas and air, and therefore the mass of the mixture. Hence we often find that the expansion parts of successive indicator-diagrams do not coincide. The law

$$p=\mathrm{M}l^{-1\cdot479}\{\kappa'+n\lambda-\sqrt{(\kappa-n\lambda)^2+s}\},$$

where κ', κ, and n are constants, satisfies all the diagrams.

n is a constant whose value depends on the point in the stroke at which the maximum pressure occurs ; and this, for a given speed of engine, depends principally on the proportion of gas to air in the mixture;

M is a constant which depends on the recentness of the last explosion.

7. *Simple Formulæ for the Ignition and Expansion parts of the Diagram.*—The complete formula (3) assumes no want of continuity in proceeding from the ignition to the expansion part of the diagram. For the sake of ease in practical calculations we may, however, assume that the ignition- and expansion-curves are quite discontinuous, employing some method of indicating continuity when results are plotted on squared paper. In this case we assume that the lines of fig. 3 are quite straight, so that

the ignition part of curve is $(a+b\lambda)\kappa l^{-m}$, . . (4)

the expansion part of curve is κl^{-m}. . . . . (5)

In our diagrams,

$$\kappa=145\cdot5,\quad m=1\cdot479\,;$$

Also $a=0\cdot257.$

In curve A B C D, $b=4\cdot372$;

" A E D, $b=1\cdot457$;

" A F D, $b=0\cdot782$;

" A G H, $b=0\cdot313$.

To use formula (4) in any given case. Find by the method already given in § 4 the constants of equation (5) to the expansion part. Assume that the ignition is complete when $\lambda=\lambda_1$. Let the pressure at the beginning of the stroke be p_0; calculate the value of κl^{-m} when $\lambda=0$, that is, when l=clearance or l_0, say; then

$$p_0\div\kappa l_0{}^{-m} \text{ is } a,$$

and

$$a+b\lambda_1=1\,;$$

so that

$$b=\frac{1-a}{\lambda_1},$$

or

$$a=\frac{p_0}{\kappa}l_0^m \text{ and } b=\frac{1-\dfrac{p_0}{\kappa}l_0^m}{\lambda_1}.$$

8. *The Rate at which the Fluid receives Heat as calculated from its Volume and Pressure.*—We shall now proceed to calculate the heat received by the fluid. This we shall do as if, instead of there being combustion going on among the particles of the fluid, we had the fluid a perfect gas receiving heat from a great number of little furnaces, or pieces of hot wire immersed in the fluid. Besides the heat here considered we have the heat radiated to the cold cylinder.

If A is the area of the piston in square inches, p the pressure of the fluid in pounds per square inch, and l the distance moved through by piston in feet, the work done by the fluid on the piston in an element of length dl is

$$\mathrm{A}p\,dl \text{ foot-pounds.}$$

It is evident that if we represent the heat which is received by the fluid in the length dl by

$$\mathrm{A}q\,dl \text{ foot-pounds,}$$

we may regard q as the rate (per foot-travel of the piston) at which heat is received by the fluid, just in the same sense as p the pressure is the rate at which work is done by the fluid; and a comparison of q and p shows at once the comparison between the rates at which heat is being received and work is being done.

Now, since we consider the fluid to behave like a perfect gas, we know from thermodynamics that

$$q=\frac{1}{\gamma-1}\left(\gamma p+l\frac{dp}{dl}\right), \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $\gamma=1{\cdot}37$ (see §§ 3 and 4); and it is obvious that the relation of p to q is not altered in any way by altering the scale to which l or p is represented in the indicator-diagram.

We have taken three methods of drawing the curve whose ordinate is q. In the first method a list of the values of p was made out from careful measurements of the curve ABCD (fig. 1), for values of l, 0·889, 0·9, 0·911, 0·922, 0·933, 0·944, &c. The observed increment of p divided by the increment of l was taken to represent the value of $\frac{dp}{dl}$ for the mean value of l. In this laborious way q was obtained for many values of l, and the curve E F G H (fig. 4) represents our result. It is obvious that the rate at which the fluid receives heat is greatest at the very beginning of the stroke, falling off during the ignition period, much more rapidly at the end of the ignition period ; and in G H we see that the fluid is losing heat during what we call the expansion part of the stroke. In the same figure the actual indicator-diagram is shown in A B C D, the pressure being shown to the same scale as the ordinate of the heat-diagram.

The area between E F G H, the line Oλ, and any two ordinates, shows in foot-pounds the heat given to the fluid between the two positions, to the same scale as that to which the area of the indicator-diagram represents work done.

Another method which we have taken is this. To find q corresponding to a point S (fig. 5) on the indicator-curve. Draw a tangent S R to the indicator-curve, meeting the line O P in R. O P and O L are the lines O P and O L of fig. 1. Draw from R a line R Q parallel to O L, meeting the ordinate from S in the point Q. Then the distance S Q, or rather TS$-$TQ, represents

$$l\,\frac{dp}{dl}.$$

Measuring S Q, therefore, paying attention to the fact that it may be negative or positive, adding to it γ times S T and dividing by $\gamma-1$, we obtain the ordinate q of the heat-curve.

Another method is to calculate q as given in (6), by actual differentiation of p as given in (3). We have employed this method, and believe that our result, in which the early part of the curve E F (fig. 4) is less steep than there shown, is probably more nearly true than what is given in fig. 4. We do not put our result forward at present because there may be a discontinuity in the explosion part of the curve, as Table VII. shows that at $\lambda = {\cdot}061$ the empirical formula does not give the observed pressure; and until we know how to eliminate vibrational effects of the indicator-spring, we have preferred only to publish the curve E F G H which has been obtained from the actual diagram, the expansion part only having been corrected for vibrations. As we know that the expansion part follows a law

$$p=\kappa l^{-m},$$

it is obvious that

$$q=\frac{\gamma-m}{\gamma-1}p,$$

being proportional to the pressure. Now, comparing this result with the part G H (fig. 4), we see that G H is not quite correct, although determined from most careful measurements of the indicator-diagram. We see here an illustration of the great importance of obtaining a formula such as that given in (3) for the shape of the indicator-diagram.

9. *Total Heat and Work of One Cycle.*—The integral of $q \, . \, dl$ multiplied by the area A of the piston in square inches gives the total heat received by the fluid during any part of the stroke, and is evidently

$$\mathrm{A}\int_{l_1}^{l_2} q \, . \, dl=\frac{\mathrm{A}}{\gamma-1}(p_2l_2-p_1l_1)+\mathrm{A}\int_{l_1}^{l_2} p \, . \, dl.$$

Taking from the diagram

$$p_1=44{\cdot}5,\quad l_1=\cdot 889,$$

$$p_2=49{\cdot}0,\quad l_2=2{\cdot}089,$$

so that $l_2-l_1=1{\cdot}2$ foot (l_2 corresponds to the part of the stroke at which the exhaust-valve opens), it is evident that

$$\int_{l_1}^{l_2} q \, . \, dl=169{\cdot}5+\int_{l_1}^{l_2} p \, . \, dl. \quad . \quad . \quad . \quad . \quad (7)$$

Or if q_m is the mean value of q during this portion of the stroke, and if p_m is the mean value of p, then

$$1{\cdot}2\,q_m=169{\cdot}5+1{\cdot}2\,p_m,$$

or

$$q_m=141{\cdot}25+p_m.$$

We find from the diagram that $p_m=94{\cdot}5$, so that $q_m=235{\cdot}75$.

Now $1{\cdot}2\,\mathrm{A}q_m$ is H, the total heat given to the fluid to alter its volume and pressure until the exhaust-valve opens;

$1{\cdot}333\,\mathrm{A}\times 61{\cdot}52$ is the indicated work W of the cycle, as calculated from the total indicator-diagram, including the dismission and suction parts not shown in fig. 1.

Hence $$\mathrm{H}=\frac{1{\cdot}2\times 235{\cdot}75}{1{\cdot}333\times 61{\cdot}52}\mathrm{W}, \text{ or } 3{\cdot}45\,\mathrm{W}.$$

As we know that combustion, about the period of opening of the exhaust-valve, is just sufficient to supply the loss by radiation to the cylinder without having much effect on the volume and pressure of the fluid, we can assume that any combustion after that time produces heat which is radiated to the cylinder. We are told that there is no combustion in the exhaust. For the small amount of combustion after the exhaust-valve opens we do not see our way at present to the basis of any but the very roughest assumption, and we think that attention ought to be paid to this matter in future investigations. What complicates the question is the fact that the mass of the fluid which radiates heat to the cylinder rapidly gets less after the exhaust-valve opens. To obtain a first approximation, we may assume that the heat of combustion after the exhaust-valve opens is equal to the work done in the forward stroke after that time—that is, 0·14 W.

The heat retained by the fluid is $141{\cdot}25 \times A \times 1{\cdot}2$, or 1·94 W.

The gases in the exhaust-pipe close to the cylinder are known to have a temperature not much greater than 400° C. Hitherto it has been customary to calculate the amount of heat carried off by the gases through the exhaust-pipe from the heat-capacity multiplied by the difference of temperature from that of the atmosphere. It must be remembered, however, that the total heat of combustion of coal-gas contains the latent heat of the steam produced, and that the exhaust gases carry off this heat. Hence the amount of about 0·95 W, deducible from the experiments of Messrs. Brooks and Steward, must be increased by two thirds of itself, giving 1·57 W as the energy carried off by the gases in the exhaust-pipe.

Hence $(1{\cdot}94-1{\cdot}57)$ W, or 0·37 W, is the amount of energy which is lost by the fluid from the opening of the exhaust-valve until the fluid is passing along the exhaust-pipe outside the cylinder. This is largely expended in heating the cylinder itself, in friction at bends in the exhaust-valve, &c.; so that it disappears as radiated heat, and as heat given to the water-jacket during the remaining parts of the cycle. Now we may safely take it that the expenditure of gas is about 22 cubic feet per hour per indicated horse-power; so that, using the heat of combustion calculated in Table I., the total energy of combustion of the gas used is 5·91 W ; and we are now in a position to make the following table. Of the 5·91 W, the total energy of combustion of a charge, we have:—

1·38 W. Work of forward working-stroke till exhaust-valve opens.

0·14 W. Work of forward working-stroke after exhaust-valve opens.

2·31 W. Heat given to the cylinder during forward working stroke by radiation before exhaust-valve opens*.

0·14 W. Heat of combustion after exhaust-valve opens and which is radiated to the cylinder.

1·57 W. Heat carried off by gases in exhaust-pipe.

0·37 W. Given to the cylinder as heat after the exhaust-valve opens, partly by friction at the exhaust-valve, partly during the succeeding three fourths or non-working parts of the cycle.

It is found by experiment that the water from the water-jacket carries off somewhat more than 50 per cent. of the total heat of combustion, or 2·96 W; but it is almost impossible to make this measurement accurately for one cycle. It is sometimes as much as 62 per cent. and sometimes as little as 35 per cent. We have not employed such a measurement here, partly for this reason, and partly on account of the rate of loss during three fourths of the cycle being indeterminate. Again, the cylinder loses heat by radiation as well as by the water-jacket; so that, even if we could assume that such a number as 50 per cent. is correct, we are still not in a position to state the total loss of heat from the cylinder.

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* It may be well to state here that we do not know with certainty the amount of gas used per indicated horse-power when the particular diagram which we are discussing was being taken, nor are we quite sure that Mr. Clerk is right in saying that the exhaust-gases show complete combustion when the engine is working to its full power. Our arrangements for determining this latter point are now nearly complete. We consider that there was no possibility of the expenditure having been less than 20 cubic feet per hour per indicated horse-power when our diagram was taken; and if we take 24 as a higher limit, and assume with Mr. Clerk that combustion is complete in the exhaust-pipe, we find the amount of heat given to the cylinder during the forward-working stroke by radiation before the exhaust-valve opens could not have been less than 1·77 W, the higher limit giving 2·85 W.

It is to be remembered that W is the indicated work. The useful work of a gas-engine, given out by the crank-shaft, is about 0·8 W, there being an expenditure of 0·2 W in overcoming the mechanical friction of the engine.

10. It is unnecessary to put before the Society the curves obtained by us by employing (6) on the discontinuous expressions of § 7 for the indicator-diagrams.

11. *Rate of Loss of Heat by the Fluid during Compression.*—For the compression part of the diagrams,

$$\gamma = 1{\cdot}385,$$

and

$$p = 39{\cdot}36\, l^{1{\cdot}304}.$$

Rate at which heat is received by fluid is $-q$, if

$$q = \frac{1}{\gamma - 1}\left(\gamma p + l\frac{dp}{dl}\right);$$

and by § 8,

$$-q = \frac{36{\cdot}36\, l^{1{\cdot}304}(m-\gamma)}{\gamma - 1}$$

$$-q = l^{1{\cdot}304}\, 39{\cdot}36 \times \frac{m-\gamma}{\gamma - 1},$$

$$m - \gamma = -{\cdot}081,$$

$$\gamma - 1 = {\cdot}385.$$

Therefore the rate at which heat is received by fluid is

$$-0{\cdot}2104\, p,$$

being proportional to the pressure, and is negative—that is, the fluid is radiating heat to the cylinder.

12. *Rate at which Fluid radiates Heat to cold Cylinder.*—It was found by the pyrometric measurements of Messrs. Brooks and Steward that the temperature of the products of combustion in the clearance-space, if there has been a recent explosion, is about 410° C.; and for the purpose of determining the temperature of the fluid before compression, they take 1·4 volume of coal-gas and 9·25 of air at 22° C. with 7·94 volumes of products of past combustions at 410° C., from which, assuming that the specific heats of the constituents do not alter with temperature, they find that the temperature of the mixture before compression is 120° C. This is sufficiently correct for our present purpose, and if we take it as the tempe-

rature when $l=2{\cdot}222$, $p_0=14{\cdot}7$, we can find the temperature corresponding with any point of any of the indicator-diagrams. We have made the calculations for various points on curve A B C D (fig. 1), knowing that $pl \div T$ is constant (see § 3).

Table VIII.

l.	p.	Absolute temperature. T.	Temperature of fluid. $t°$ C.	$t° - 60°$ C.	Ordinate of semicircle.	Ratio.
·889	44·5	476	203	143	0	∞
·949	86	982	709	649	28	23·18
·989	105	1244	974	914	35·5	25·74
1·089	126	1644	1371	1311	48	27·33
1·389	90	1496	1223	1163	65	17·89
1·689	66	1344	1071	1011	66	15·32
2·089	49	1231	958	898	40	22·45

From some diagrams examined by us we find that the fluid may have as high a temperature as 1900° C.

The temperature of the water leaving the water-jacket was about 60° C.; and we may for our purposes assume that the rate at which the fluid loses heat to the cylinder is proportional to the excess of its temperature above 60° C., so that $t-60°$ represents, to some scale, the fluid's loss of heat to the cylinder per second. This rate of loss is shown on the curve A B (fig. 6).

Now if H is the quantity of heat which has been given by the fluid to the cylinder-jacket at the time τ, then $\dfrac{dH}{d\tau}$ is represented by the ordinate of the curve A B. But

$$\frac{dH}{d\lambda}=\frac{dH}{d\tau}\frac{d\tau}{d\lambda} \text{ or } \frac{dH}{d\tau}\div\frac{d\lambda}{d\tau};$$

and as the piston-motion is very nearly

$$\lambda=r(1-\cos a\tau),$$

$$\frac{d\lambda}{d\tau}=ra\sin a\tau;$$

that is, $\dfrac{d\lambda}{d\tau}$ is proportional to the ordinate of a semicircle C E F. Describing the semicircle C E F with a diameter equal to the length of the stroke, and dividing the ordinates of A B by those of C E F, we obtain the curve G H I, whose ordinate at any point represents the rate of the fluid's loss of heat to the cylinder per foot of piston-motion; so that the whole area C G H I F represents the total loss of heat to the cold cylinder during the stroke. We are in a position to speak of the loss of heat from $\lambda=0$ to $\lambda=1{\cdot}2$ (see § 9).

This loss must be represented on the diagram to the same scale as the indicator-diagram represents work done, and it is expended in the part of the working stroke from $\lambda=0$ to $\lambda=1{\cdot}2$. Hence if k is the mean ordinate of such a diagram,

$$k=2{\cdot}31\times 61{\cdot}52\times 1{\cdot}330\div 1{\cdot}2=158.$$

Now the mean ordinate of the curve G H I (fig. 6) from $\lambda=0$ to $\lambda=1{\cdot}2$ being taken and found different from 158, all the ordinates of G H I (fig. 6) have been diminished in the proportion of 158 to the mean ordinate of G H I (fig. 6) to get the diagram X L Y of fig. 4. This diagram X L Y represents the rate of loss of heat by conduction and convection from the fluid to the cylinder during the working stroke until the exhaust-valve opens.

13. *Rate at which Combustion goes on during the Stroke.*—The curve E F G H represents the rate at which heat is actually gained by the fluid, and X L Y shows the rate at which heat is wasted to the cylinder; so that the curve I J K Y shows at every point the rate at which heat is being generated in the fluid by combustion. It is obvious, then, that combustion is not complete at the end of the explosion part of the curve, although, as Mr. Clerk's experiments prove, the mixture of air and gas is in the proper proportions for explosion immediately behind the piston at all periods of the compression-stroke. The diagram I J K Y is specially valuable, as showing the effect of dissociation of the products of combustion at such temperatures as obtain in the gas-engine, and are shown in Table VIII.

Postscript, *added June* 10th.—We have assumed in the paper that the rate of loss of heat by radiation and convection is proportional to the difference between the mean temperature of the fluid and the temperature of the cylinder. When we have more information concerning the distribution of heat in the fluid, and the way in which a heated fluid loses its heat to a cold enclosing vessel, a more accurate assumption may be made; and it is easy to see what alteration this will introduce in our method of obtaining the curve X L Y (fig. 4).

It is known from the experiments of MM. Dulong and Petit that the rate of cooling by radiation and convection of a solid body increases more rapidly than the difference of temperature, and that it is greater at greater pressures of the gaseous medium between the hot body and the surrounding cold vessel.

We are now engaged in an investigation involving much higher differences of temperature than those of MM. Dulong and Petit; and in so far as we have obtained results for temperatures extending from about 800° C. to 1300° C., we have confirmed the conclusions of these gentlemen. Thus the loss of heat per second at 776° C. being 97·2, the loss at 1292° C. is 253·2.

Our method of experimenting is, we believe, new. The heated body is a spiral of platinum, whose change of electric resistance when there is change of temperature is known. It is surrounded by a vessel, blackened inside and maintained at constant temperature. An electric current is made to pass through the platinum spiral, maintaining it at any required temperature. An ammeter and voltmeter enable the current A and the difference of potentials V between the ends of the platinum spiral to be measured. Then VA is the rate at which heat is being radiated from the platinum, and V / A is the electric resistance of the platinum, from which its temperature is known. We intend to investigate the influence of high pressures of air and other gases.

We are somewhat doubtful as to the weight which we ought to give to the results obtainable from these experiments on the loss of heat by solid bodies, since in our gas-engine investigations we deal with a mixture of hot gases; and in adopting the law of simple proportionality to difference of temperature, we have been influenced by the fact that rate of loss of heat by the fluid in the compression-stroke increases much more slowly than is indicated in Dulong and Petit's law, although the pressure of the fluid is increasing as well as its temperature. The result given in § 11 is to the effect that during compression the rate of loss of heat by the fluid is nearly proportional to the $\frac{1}{2}\frac{3}{3}$ power of the absolute temperature of the fluid, or to

$$(\theta+333)^{\frac{1}{2}\frac{3}{3}},$$

if θ is the difference of temperature from 60° C., the temperature taken as that of the cold cylinder. If q is this rate of loss, it is obvious that $\frac{dq}{d\theta}$ diminishes as θ increases. It will be observed that the probability of the piston's having a high temperature causes this result to be even more curious than it might otherwise appear to be.

PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

SEPTEMBER 1884.

XIV. *On Salt-Solutions and Attached Water.*

By FREDERICK GUTHRIE [*].

VIII.

[The paragraphs are numbered in sequence with those of my memoir on Eutexia, *anteà*, p. 146.]

§ 232. *Introduction.*—When, some ten year sago, the first experiments in this subject were brought before the Physical Society, it was pointed out that the key to the temperature of any salt-ice freezing-mixture was to be found in the temperature of fusion of the cryohydrate of that salt. Since then further light has been thrown upon the subject by the discoveries and observations of others. Thus, Ditté has obtained a hydrate (probably a subcryohydrate) of hydrochloric acid, and Wroblewski has obtained a similar hydrate of carbonic acid. Pettersson, in his exhaustive study of marine ice, made in the 'Vega' expedition, has explicitly admitted that the phenomena presented by freezing and frozen sea-water can only be satisfactorily explained by the formation and properties of the cryohydrates. Though this tacit corroboration or explicit adoption by foreigners of the views I ventured to advance has given me perhaps more satisfaction than if they had been only accepted by English physicists, I may be allowed to express some regret that the latter do not yet appear to be awake to the interest and importance of the subject. It gives me, therefore, unusual pleasure to offer them this my eighth memoir on this branch of Molecular Physics.

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[*] Read May 24, 1884.

In this memoir I shall first make a study of the ammonia group in its behaviour with water. I add a little to our knowledge of ammonia itself in this respect. Then are examined the effects of replacing one or more of the hydrogen equivalents by ethyl. Then will be described in some detail the behaviour with water of some aniline salts.

Secondly (§§ 249–255), I shall shift the region of my inquiry upwards on the thermometric scale, and include in it temperatures at which the solid fuses *per se*, and shall thus establish the continuity of the phenomena of fusion with those of solution, making clear the fact that certain bodies, originally solid, may at high temperatures become miscible with water in all proportions. It will be shown how this latter branch of the inquiry, apart from its purely physical interest, has a great geological one, as it throws light on the pyrohydration of igneous formations, just as the cryohydration in floes has thrown light on the formation of those masses.

§ 233. *Ammonia.*—Anhydrous ammonia, NH_3, according to Faraday becomes solid under a pressure of 20 atmospheres at a temperature of $-75°$ C. According to Fourcroy and Vauquelin, a perfectly saturated solution (? saturated at air-temperature) freezes between $-38°$ and $-41°$ C., forming shining flexible needles; at $-49°$ C. it freezes to a grey gelatinous mass.

Starting with a 33·3-per-cent. solution, I made solutions of various strengths, and found that pure ice separated from them at the following temperatures:—

TABLE XLV.

Showing Separation of Ice from Solution of Ammonia.

Per cent. of NH_3.	Per cent. of water.	Temperature of beginning solidification.	Body separated.
1	99	$-0°.8$	Ice.
3	97	-3.2	"
5	95	-5.6	"
10	90	-12.8	"
15	85	-21.4	"
20	80	-43.4	"

Judging by the analogy, which will appear more clear in the sequel, it seems that the body mentioned by Fourcroy is a subcryohydrate, and that the gelatinous mass mentioned still contained too little water for the cryohydrate. I find that a 33·3-per-cent. solution does not crystallize at $-80°$ C.; and I have as yet been unable to obtain the true cryohydrate.

§ 234. *Ethyl-Ammonias.*—The ammonias whose relationship to water have next to be described were obtained from Kahlbaum of Berlin. They were verified by means of their boiling-points, their platinum double chlorides, and by titration with standard hydrochloric acid. Those which I here employ were found to be pure.

§ 235. *Ethylamine.* Boils at 18° C.—The solutions of this base were made by dropping an indefinite quantity into a narrow-necked weighed bottle, putting in the stopper, weighing, surrounding by a freezing-mixture, and running in the proper quantity of distilled water from a burette. When the quantity of water was small, it was dropped in from a capillary tube until the proper weight was reached.

The first five solutions, namely those containing 0·99, 5, 10, 15, and 20 per cent. of ethyl-ammonia ($NH_2C_2H_5$), showed, on cooling, the separation of the easily recognizable ice-crystals. On further cooling the 20-per-cent. solution, the separating crystals became opaque, betraying the cryohydrate; this occurred at $-13°.9$, whereupon the temperature became stationary. After ten or twelve grams had solidified at $-13°.9$, the remaining liquid was poured into a fresh tube and reduced to the same temperature. The same operation having been performed three times, the liquid was considered pure; 3·589 grams of it were weighed in a stoppered bottle, diluted with water, over-neutralized with hydrochloric acid, evaporated in a water-bath in a platinum dish until the chloride became quite hard on cooling, heated to incipient volatilization, and weighed. There was thus obtained 1·3415 gram chloride of ethyl-ammonium or 0·7407 ethylamine, which corresponds to 20·64 per cent.

On cooling a stronger solution than this, solidification begins at a higher temperature, reaches a maximum between 30 and 35 per cent., and again falls, passing out of the range even of a solid carbonic-acid cryogen. As there is only one tenth of a degree difference between the points of initial solidification of the 30- and 35-per-cent. solutions, and guided by the general shape of the curve, I made a 32·4-per-cent. solution, and found that solidification began at −8° C.

It is well known that anhydrous ethylamine is not solidifiable in a solid carbonic-acid cryogen. Accordingly, the solid which separates from an aqueous solution of ethylamine of any and every strength between −13°·9 and the anhydride is one of those remarkable bodies which I have called subcryohydrates, and which have been observed in the chloride and iodide of sodium.

The subcryohydrate of ethylamine, as a glance at the curve (fig. 1) will show, has a solidifying-point within certainly one tenth of a degree C. of −8°, and, as certainly, it has within two or three tenths of a per cent. the composition of 32·4 per cent. It is minutely crystalline, and of nearly the same specific gravity as the residual liquid. Its solution is eminently supersaturable, and in that state is curiously viscid. It is not easy to see a way whereby it might be made to purify itself in the act of formation. The existence of these solid hydrates of a substance which by itself resists solidification by a carbonic-acid cryogen, and the fact that their melting-points are only ten degrees or so below 0° C., is surely an unanswerable argument that they are not mere juxtapositions of independent crystals of the two constituents.

Any horizontal line between −13°·9 and −8° cuts the curve of aqueous ethylamine in three places. Within these limits, therefore, there are always three degrees of strength of the solution, which begin to solidify at the same temperature.

Thus, if we find an aqueous solution of ethylamine begin to solidify at −12°, we do not know whether it is of the strength 18·7 or 22·2 or 43·3 per cent. Further, it may be noted that, on adding water of the air-temperature to the solid subcryohydrate, a depression of temperature occurs to a point lower than that at which the subcryohydrate stood.

TABLE XLVI.

Separation of Solids from Aqueous Solution of Ethylamine.

Per cent. of Ethylamine.	Per cent. of water.	Temperature at which solidification begins.	Nature of solid.
*0·9901	99·01	−0°·4	Ice.
5	95	− 2·0	,,
10	90	− 4·7	,,
15	85	− 8·4	,,
20	80	−13·3	,,
20·64	79·36	−13·9	Cryohydrate.
25	75	− 9·5	Subcryohydrate.
30	70	− 8·1	,,
32·4	67·6	− 8·0	,,
35	65	− 8·2	,,
40	60	−10·1	,,
50	50	−16·4	,,

§ 236. *Diethylamine.*—Let us now replace another equivalent of hydrogen by the same organic radical, and examine the relation towards water of diethylamine, $NH(C_2H_5)_2$. This liquid boils at 54° (57°, Hofmann) at 31·02 B. The solutions were prepared precisely as in the preceding case.

The four weakest solutions, which contained 5, 10, 15, and 20 per cent. of base respectively, gave no trouble. But from this point the curve (fig. 1) descends very sharply towards the cryohydrate, and rises again with equal steepness. A 22-per-cent. solution yields ice on incipient solidification at 9°·9; while a solution containing only 1 per cent. more, a 23-per-cent. solution, yields subcryohydrate at the same temperature of 9°·9. To this difficulty has to be added the circumstance that I have not met with a substance which shows so extraordinary an aptitude for supersaturation. The solutions of the subcryohydrate in the anhydrous base (all those to the right of the cryohydrate in fig. 1) and the cryohydrate itself may be cooled to −20°, and diligently stirred without showing signs of solidification. The solidification may then be started by a cryogen of solid carbonic acid and ether. Moreover, the solutions near the saturated conditions are as viscid as glycerine; so that the appeal from one part of the liquid to another in the matter of crystallization, and consequent change of composition of the residual liquid, is tardy. These circumstances made it impossible to obtain the cryohydrate pure for analysis in the ordinary way by automatic purification. But they also made it unnecessary; for since a 22 per cent. gives up ice and a 23 per cent. gives up subcryohydrate at the same temperature (9°·9), it follows that a 22·5-per-cent solution must, within a probable error of about 0·2 per cent., have the composition of the cryohydrate. Having made such a solution, and cooled it to −10° in a salt-ice cryogen, the bottom of the tube containing it was dipped in a little carbonic-acid cryogen until a little white opaque regulus of crystals was formed. The whole being then restored to the ice-salt cryogen and stirred, opaque solidification began, the rounded tufts of crystals much resembling oatmeal in suspension. From first to last the temperature now remained constant at 11°·0 C. Of course there was no need to analyze a body thus synthesized.

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* Accidentally taken 1 to 100, instead of 1 to 90.

TABLE XLVII.

Separation of Solids from Aqueous Solution of Diethylamine.

Per cent. of Diethylamine.	Per cent. of water.	Temperature of initial solidification.	Nature of solid.
5	95	−1°·1	Ice.
10	90	2·9	,,
15	85	5·2	,,
20	80	8·4	,,
21	79	9·1	,,
22	78	9·9	,,
22·5 (±0·2)	77·5 (∓0·2)	11·0	Cryohydrate.
23	77	9·9	Subcryohydrate.
25	75	9·1	,,
30	70	8·3	,,
35	65	8·0	,, (pure)
40	60	8·2	,,
45	55	8·6	,,
50	50	9·1	,,
60	40	12·2	,,
70	30	23·4	,,

Diethylamine does not solidify in a carbonic-acid cryogen.

§ 237. *Triethylamine*, $N(C_2H_5)_3$. Boils at 88°.—Viewed as an anhydride, we should expect, *à priori*, to find a greater difference between the physical properties of this body and those of diethylamine than between those of the latter body and ethylamine. Indeed, the difference might be expected to be comparable with that existing between the properties of ethylamine and those of ammonia; for the replacement of the first and the last equivalent of hydrogen by ethyl would be expected to effect a difference of kind, while the replacement of two instead of one would effect rather an alteration in degree. Be this as it may, the properties of triethylamine in reference to water are quite exceptional, or at least very remarkable. The solutions of strengths 5, 10, and 15 per cent. yielded ice; the latter and the 20 per cent. can be employed for obtaining the cryohydrate, but the 20 per cent. begins its solidification with the subcryohydrate. The solidifying temperature of the cryohydrate is $-3°\cdot8$ C. This cryohydrate contains 19·15 of the anhydrous base. It may be remarked that the hydrochloride of this base retains hydrochloric acid with such firmness that, even when heated to incipient volatilization, it still remains acid [*].

The subcryohydrate of this body is, like those of the previously examined ones, very prone to supersaturation; so that, in examining the richer solutions, it is advisable to have recourse to the solids of previous preparations; which act like a ferment. A nearly remelted tubeful of the subcryohydrate, set to resolidify very slowly, crystallizes in bright laminæ one or two millimetres in diameter. More quickly frozen in repose, crystalline masses an inch long are fashioned upon the glass.

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[*] A few grains of chloride of triethyl-ammonium heated on a hot spatula exhibit a beautiful phenomenon. The columns and whirls of white smoke can be watched petrifying in the air to white soot without much change of form.

TABLE XLVIII.

Separation of Solids from Aqueous Solutions of Triethylamine.

Per cent. of Triethylamine.	Per cent. of water.	Temperature of initial solidification.	Nature of body formed.
5	95	– 1°·0	Ice.
10	90	– 2·0	,,
15	85	– 2·9	,,
18	82	– 3·4	,,
19·1	80·9	– 3·8	Cryohydrate.
20	80	– 3·5	Subcryohydrate.
30	70	– 4·1	,,
40	60	– 5·1	,,
50	50	– 6·7	,,
70	30	–13·6	,,
80	20	–20·6	,,

For the curve, see fig. 1, p. 179.

§ 238. Triethylamine is one of those rare bodies which, like sulphate of sodium, sulphate of calcium, caustic lime, and a few others, are more soluble in cold than in hot water. The behaviour of the three bodies named is clearly traceable to the decomposition by heat of definite hydrates. Without laying undue stress upon this, it seems that the phenomenon in question is one of decomposition, which so often follows increased temperature, and not an inversion of the rule that solubility also increases with temperature. The body decomposed in the case before us is clearly a hydrate—either the cryo- or subcryohydrate. Accordingly, though striking in its presentation, the phenomenon is really quite continuo with the decomposition by heat of oil of vitriol; which decomposition, I presume, does actually take place when that liquid is heated above its boiling-point (in a closed vessel). But while in the latter case the products of decomposition are probably miscible, and mix, though held apart from chemical union by heat-tension, with the hydrates of ethylamine the products of thermal decomposition are separated not only chemically but in mass, because, when chemically separated, they are not molecularly miscible, at least in all proportions.

The following table shows the temperatures at which turbidity begins and ceases in aqueous solutions of triethylamine of various strengths. (See also fig. 1, "Triethylamine and Water as liquids.")

TABLE XLIX.

Separation in Aqueous Solutions of Triethylamine.

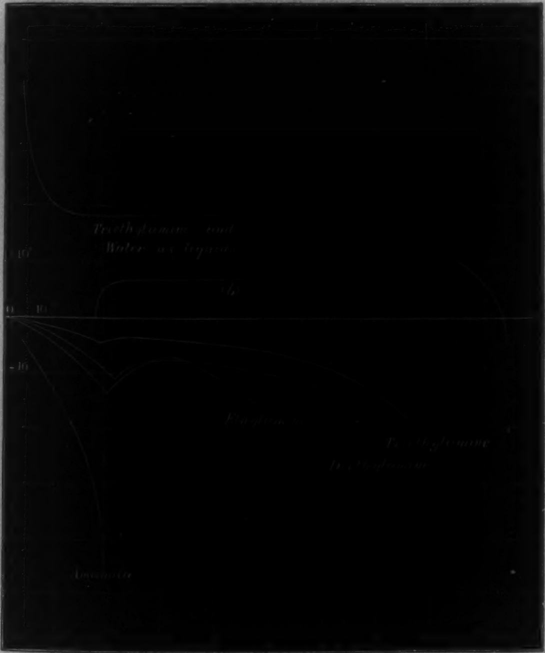
Per cent. of Triethylamine.	Per cent. of water.	Critical temperature between clearness and turbidity.	Remarks.
1·96	98·04	78°	Becomes clouded, and begins to boil.
3·85	96·15	41	
5	95	34	
8	92	23·5	
10	90	21·3	
15	85	18·8	
18	82	18·6	
20	80	18·6	
30	70	18·2	
40	60	18·4	
46·46	53·54	18·3	
50	50	18·4	
70	30	17·1	
80	20	13·4	
90	10	6·1	
94·5	5·5	−7 (about)	
99	1	......	Complete liquid solubility at all temperatures.

A solution containing only 0·99 per cent., sealed in a very strong glass tube and heated to 200° C., did not show any opalescence.

A 1·96-per-cent. solution begins to give off bubbles of gas at the same temperature at which it becomes turbid. A still more dilute solution, namely a 0·99 per cent., does not become turbid at 200° C., when it is heated in a sealed tube. The curve (fig. 1, "Triethylamine and Water as liquids") shows the relationship above examined. The following example illustrates the history of a solution. Ten grams of ethylamine and 90 grams of water, shaken together at 25°, form a white emulsion. On standing at that temperature, two transparent layers are formed, of which the upper is ethylamine saturated at 25° with water, and the lower water saturated at 25° with ethylamine. On heating to 28°, both layers become turbid; the upper sheds water saturated at 28° with ethylamine, which falls, and the lower ethylamine saturated at 28° with water, which rises. These new quantities join their respective camps, the constitution of which has, of course, been altered by the departures, and is now that of saturation at the new temperature in the two cases. The surface of demarcation shifts towards the centre of the mass. Similar effects follow further rises of temperature. Let now the tube cool. The former condition is reestablished. On further cooling, the surface of demarcation shifts—rises in this case as the two liquids mix more with one another. At 21°·3 perfect solution ensues, and this is well marked within a tenth of a degree. Just above this temperature the mass is opalescent, just beneath it it is perfectly limpid. When at this critical temperature, the warmth of the hand only momentarily applied makes a wide test-tube of the limpid mixture quite milky. Nor can such a test-tube be passed so nimbly through a flame as not to exhibit the same change. Following the temperature downwards, we find the solution remains clear below 0°, until we reach — 2°, whereupon crystals of ice appear. These increase with the falling temperature until — 3°·8 temperature and 10·1 per cent. is reached. The cryohydrate now solidifies, and no further percentage change is possible; nor temperature change, until solidification is complete.

A 40-per-cent. ratio only shows perfect mixture at 18°·4. It remains a mixture until —5°·1, whereupon subcryohydrate begins to appear in the solid form. Its quantity goes on increasing with lowering temperature until —20°·6 is reached: this marks an 80-per-cent. solution. At still lower temperatures no doubt the liquid becomes more enriched. If the anhydrous liquid is unsolidifiable by cold, then the ordinate at 100 per cent. is asymptotic; but if, as is more likely, the liquid is solidifiable, the remainder of the water and of the ethylamine will unite to form some hydrate even lower than the subcryohydrate at some very low but constant temperature. An 80-per-cent. ratio at — 30° is thick with solid subcryohydrate. Perfect liquefaction takes place at — 20°·6. The liquid remains clear until + 12° is reached. At and above 12° separation ensues, which increases with the increasing temperature. The curve (fig. 1, "Triethylamine and Water as liquids") is virtually a straight line between 15 per cent. and 50 per cent. The deviations are probably errors of observation; and these errors of observation are certainly not due to want of definition of the occurring and vanishing turbidity, which is well marked within 0·025 of a degree. Nor are they due to errors of original weighing or change during manipulation; for the very flatness of the curve shows that a great change of composition has little effect upon the temperature of saturation. If they are indeed errors, they arise probably from the collecting together of the opalescing globules into clear drops which separate down, leaving the liquid above as clear as though it had been cleared by cold. The indication from a gradually ascending temperature is accordingly more to be relied on than one from a falling temperature.

Fig. 1.



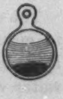
When water is added to triethylamine, but little heat is evolved. A very small rise in temperature occurs when the 30-per-cent. mixture is made. The constituents should be brought to about 10°; and in the final experiment the thermometer and thin glass bulb, in which the mixture is effected, are to be previously warmed fully to the temperature at which they stood at the end of the previous experiment. It is probable that the smallness of the heat of combination is nearly connected with the ease of thermal separation. It is to be noticed, moreover, that in the region of the lower curve about the subcryohydrate, where the curve is flat because great change of *percentage* makes little difference in temperature of initial solidification, the curvature of the upper curve, fig. 1, "Triethylamine and Water as liquids," is also nearly nothing. Whether above or below zero, we are dealing apparently at every individual percentage with the same substance, the subcryohydrate: it is this region which is so keenly sensitive to changes of temperature.

§ 239. There is this important and essential difference between the genesis of a cryohydrate and that of a subcryohydrate. Solutions of nearly the cryohydrate strength approach the composition of that body as they lose heat and sink in temperature—weaker ones by the shedding of water (as ice), stronger ones by the shedding of salt or subcryohydrate. And this is true for all solutions from 0 per cent. up to the strength of the subcryohydrate; that is, on the curve, to the point where $\frac{dx}{dy}$ changes sign.

Not so with the subcryohydrate. A solution weaker than the subcryohydrate, to the left of it on the figure, will "run down" to the cryohydrate by dint of shedding the subcryohydrate. A solution stronger than the subcryohydrate will "run down" to the solidifying-point of the anhydrous liquid or to that of some secondary cryohydrate, no example of which is, I think, yet known. In either case, the liquid residue gets further and further away from the ratio in the subcryohydrate. The whole condition may be illustrated by the motion of a marble rolling upon the curve. It will run down to the bottom of the valley of the cryohydrate wherever it is placed on the slopes of that valley, and there remain in stable equilibrium. But placed upon the top of the great swell of the subcryohydrate, it will be at rest only if undisturbed, and so be in instable equilibrium. It will, if disturbed, either roll down to the bottom of the cryohydrate valley, or roll into the abyss of the anhydrous liquid. The cryohydrate is the level of a lake. The subcryohydrate is the watershed (subcryohydrate shed) of a hill-range.

The cryohydrate being an eutectic alloy, the subcryohydrate is a definite chemical combination, existing probably as such in the liquid when above zero, and liberating in its formation the heat observed when the two liquids are mixed; and as, for instance, sulphate of soda crystallizing either from an acid or alkaline solution leaves the liquid more acid or more alkaline than before, so the subcryohydrate in its solidification leaves the liquid from which it separates continuously more aqueous or less aqueous according as it started from a solution more or less aqueous than itself. The "more" and "less," as here employed, refer of course to intensity, not to quantity, and the change is the analogue of that suffered by electricity when the surface of a conductor alters in size.

§ 240. *Some Applications of the above Property of Triethylamine.*—It appears from Table XLIX. that one weight of triethylamine with 19 weights of water is a ratio requiring 34° C., or 93°·5 F., that is a low blood-heat, to effect its turbidity. A ratio of 1 of ethylamine and 24·76 of water requires 41° C. or 105°·8 F. for the same effect to be produced: this is a fever heat. Accordingly, a few little glass capsules containing solutions of the triethylamine of strengths graduated between these two and thereabouts, and containing also a little mercury to assist the stirring-up when shaken, may be of use in the diagnosis of fever. The eye may be fastened to a thread or rod, and so introduced beneath the arm or into the cavities. I have made a series of 9 such capsules, which show turbidity at F. 68°·3, 69°·4, 76°·1, 79°·9, 91°·4, 98°·6, 105°·2, 111°·2, 123°·8.



§ 241. The radiation from an electric arc passing into an 8-per-cent. solution will warm it to opacity. Thin strips of variously coloured glass placed in such solutions will determine the opalescence after various time lapses,—the red glass acting the slowest, and the others, speaking broadly, the quicker the shorter the wave-length of the light they transmit. Two of complementary colour, which together absorb all radiation, or a single black one, act the quickest. Coloured glasses placed between the solution and the source of radiation cause opalescence in times which are the longer the shorter are the transmitted wave-lengths.

A few drops of the solution placed as a thin film between two thin sheets of flat glass, and prevented from evaporation by sulphur-cement around the edges, forms a sensitive plate. The hand placed upon it leaves a white silhouette. The spectrum thrown upon this plate leaves a transient record.

It is probable that the heat liberated when triethylamine is mixed with water is, if the expression may be allowed, the real image of the heat which on entering the mixture effects separation. They are both equal in quantity to the heat of subcryohydration; the former being that heat itself. It is a happy circumstance that the temperature at which separation begins within the limits of 20 to 50 per cent. solutions is a usual atmospheric temperature, namely 18°·3 C. (64°·94 F.).

§ 241*a*. The quantitative relationship in respect to solubility existing between water and triethylamine was determined with considerable accuracy in the following manner. A 50 c. c. burette graduated to two-tenths was sealed at one end, and the mercury and water-meniscus values determined. It was drawn out to a narrow neck, and received about 2 c. c. of mercury. The whole being now counterpoised, a few c. c. of ethylamine were introduced, which proved to weigh 6·86 grams. A few grams of water were next added, the end sealed off and dried, and the whole reweighed. It was found that 7·885 grams of water were present.

The whole was now brought to a temperature low enough to ensure perfect mixture, and then gradually heated in a large beaker of water to which successive portions of warmer water were added. The water was diligently stirred. When the temperature is high enough to cause separation, the tube is kept at that constant temperature for half an hour, being repeatedly shaken. Taking the level of the mercury as constant, and calling it, when corrected for meniscus, 0, we have first the height of the plane of separation of the two liquids to read off. This requires no correction for meniscus at temperatures below 25° C. At 30° and 50° there is some + curvature (like water); this I have neglected. The height of the upper surface has to be read and corrected for meniscus. (For this the same correction is taken as for water.) The volume of water at 15° was 7·88 c. c., and the volume of triethylamine was 9·5 c. c. On bringing the two together, sufficient heat was set free by the mixture of part to prevent the mixture of the whole. On cooling to 15° the two mixed perfectly, and the volume was 16·6, showing therefore a contraction of 0·8 c. c. At 18°·3 the liquid still remained clear, but at 18°·7, that is in half a degree, a great separation had occurred. In the following table the corrected readings are given.

Separation between water and triethylamine (Triethylamine 46·45 per cent., Water 53·55 per cent.).

At °	Vol. of lower stratum.	Vol. of upper stratum.
15·0	0	16·6
18·3	0	16·6
18·7	3·5	13·2
19·0	4·5	12·2
20·0	6·1	11·4
21·0	6·8	10·1
22·0	7·2	9·7
25·0	7·8	9·3
30·0	7·9	9·4
50·0	8·0	9·7

So nearly complete is the separation at 25°, that above this temperature the upper stratum gives more in volume by expansion by heat than it loses by the rise of the plane of demarcation. To get an idea of the completeness of the separation at 50° C., we may compare the volume of the lower stratum at 50°, which is 8·0, with that of 7·885 grams of water at 50°, which is 7·93. This signifies that at 50° the lower stratum must be nearly pure water, and the upper nearly pure ethylamine. For the plane of separation stands only $\frac{1}{80}$ of the height of the original water-column above that height. See fig. 1, curve *b*.

§ 242. *Thermal Relation of some Aniline Salts to Water.*—In turning to organic ammonias and their salts which contain radicals of greater molecular weight, and belonging to different series from those we have been considering above, we are tempted by aniline. It can be got in a state of great purity. Its salts are well defined and stable, and of various degrees of solubility. The aniline I employed was rectified several times, converted into the chloride, and twice recrystallized; reconverted into the base by caustic potash, dried, and finally distilled.

Aniline is slightly soluble in water. On cooling to a temperature of − 0°·7, the water and aniline solidify together as a porcelain-like opaque cryohydrate, which is, however, too poor in aniline to be capable of satisfactory analysis.

§ 243. *Chloride of Aniline.*—As a cryogen, the chloride of aniline gave a temperature of −10°·5. For its solubility the weighed solution was evaporated in a water-bath until it ceased to lose weight. Saturated at 13°·1, it was found that 8·3210 grams gave 3·8875 anhydrous salt, or 46·72 per cent. Saturated at 0°, 13·2836 grams gave 5·3595 grams dry salt, or 40·35 per cent. The solution saturated at 0°, or a 20-per-cent. solution placed in a freezing-mixture, falls to the temperature of −10°·7. It is here as generally preferable to reach the cryohydrate from the dilute side. This cryohydrate readily forms a supersaturated solution. Of the cryohydrate, 7·1760 grams gave 2·2860 dry salt, or 31·86 per cent.

Percentage solutions were then made, and their temperatures of initial solidification determined.

TABLE L.

Chloride of aniline per cent. by weight.	Water per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
1	99	− 0°·2 C.	Ice.
4	96	− 1·0	,,
5	95	− 1·3	,,
6	94	− 1·6	,,
7	93	− 1·9	,,
8	92	− 2·2	,,
9	91	− 2·5	,,
10	90	− 2·8	,,
11	89	− 3·0	,,
12	88	− 3·3	,,
13	87	− 3·6	,,
20	80	− 5·7	,,
25	75	− 7·2	,,
30	70	− 9·0	,,
31·86	68·14	−10·7	Cryohydrate.
35	65	− 8·0	Salt.
40·35	59·65	0	,,
46·72	53·28	+13·1	,,

The curve corresponding to the above table is shown in fig. 2.

§ 244. *Nitrate of Aniline.*—As a cryogen, the temperature −2°·2 was obtained. A solution saturated at 13°·1 was evaporated *in vacuo* over sulphuric acid until it ceased to lose weight; 7·5174 grams gave 1·1710 gram dry salt, or 15·58 per cent. 8·6860 grams of solution saturated at 0° gave 0·9500 gram, or 10·94 per cent. A dilute solution reached, in a freezing-mixture, the constant temperature of −2°·2. Of this, the cryohydrate, 7·7972 grams gave 0·8270 gram dry salt, or 10·61 per cent. The nitrate cannot be dried in a water-bath without suffering partial decomposition. The above results are embodied in the following table, which also shows the temperatures of initial solidification.

TABLE LI.

Nitrate of aniline per cent. by weight.	Water per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
2	98	− 0°·4	Ice.
4	96	− 0·8	„
6	94	− 1·1	„
8	92	− 1·5	„
10	90	− 2	„
10·61	89·39	− 2·2	Cryohydrate.
10·94	89·06	0	Salt.
15·58	84·42	+13·1	„

Fig. 2 shows the curve representing the above numbers.

§ 245. *Sulphate of Aniline.*—This salt was recrystallized three times, and after drying between blotting-paper was finally dried before a brisk open fire. As a cryogen it showed a temperature of −0°·8. Of the solution saturated at 13°·1, it was found that 25·6925 grams gave 1·5000 dry residue, or 5·84 per cent. Of the solution saturated at 0° C., 8·8675 grams gave 0·4357 gram, or 4·91 per cent. The solidifying temperature of the cryohydrate was found to be −0°·9, and 9·5607 grams of it gave 0·4620 gram dry salt, or 4·83 per cent. This salt appears to melt in its water of crystallization, and takes a long time to dry. The following table contains the above results, together with the temperature of initial solidification in solutions of several strengths. The sparing solubility of the salt limits the table very much.

TABLE LII.

Sulphate of aniline per cent. by weight.	Water per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
1	99	– 0°·1	Ice.
2	98	– 0·2	"
4·5	95·5	– 0·6	"
4·83	95·17	– 0·9	Cryohydrate.
4·91	95·09	0	Salt.
5·84	94·16	+13·1	"
15·35	84·65	100·0	"

The curve representing this table is found in fig. 2.

§ 246. *Oxalate of Aniline.*—8·3230 grams of the oxalate of aniline saturated at 14°·5 gave 0·1080 gram dry salt, or 1·29 per cent. At 0° I obtained 0·0320 gram of the dry salt from 10·8170 grams solution, which means only 0·29 per cent. The cryohydrate was formed at the very high temperature of –0°·4. On evaporation, 8·5450 grams gave 0·02 gram dry salt, or only 0·14 per cent. The sparing solubility of the salt in water prevented me from examining solutions of strengths weaker than the cryohydrate.

TABLE LIII.

Oxalate of aniline per cent. by weight.	Water per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
0·14	99·86	– 0°·4	Cryohydrate.
0·29	99·71	0	Salt.
1·29	98·71	+14·5	"

For curve see fig. 2. Although the temperature here shown for the cryohydrate is distinctly below zero, proving that the oxalate is not, like a colloid, molecularly free from the water, yet I am not assured that I have been able to form a true cryohydrate in the solid form. The ice and salt separate apart, the former adhering to the glass, and the microscopic transparent crystals of the latter remaining in suspension in the solution. The first analysis, indeed, showed greater percentage of salt at −0°·4 than at 0°, the difference amounting to about 0·28 per cent. on the highest. This is an impossible result. The state of things clearly arose from the circumstance that the liquid cryohydrate was enriched by the suspended crystals. The solution at 0° was also abnormally rich from the same cause. It was only on keeping the solution in ice for twenty-four hours that the zero amount above given was obtained, and by keeping the zero solution for twelve hours in a weak freezing-mixture (nitre and ice) that the cryohydrate (in a liquid form) was got.

§ 247. *Salicylate of Aniline*[*].—The above remarks are again applicable to this salt. So sparingly is it soluble in water at all temperatures, and so close below 0° is the cryohydrate, that no examination of this region was practicable. Of a solution at 0°, 10·3720 grams gave 0·0295 gram, or 0·28 per cent. The cryohydrate formed at −0°·05 or −0°·07. Of it, 10·0310 grams gave 0·0245 gram, or 0·24 per cent. A solution saturated at 6°·2 gave 0·0710 gram salt out of 10·9270 grams solution, that is 0·65 per cent. Even at 16°·8 there was only obtained 0·0800 gram from 10·3450 grams, or 0·77 per cent.

TABLE LIV.

Per cent. of salicylate of aniline by weight.	Per cent. of water by weight.	Temperature at which solidification begins.	Nature of solid.
0·24	99·76	−0°·06	Cryohydrate.
0·28	99·22	0	Salt.
0·65	99·35	+ 6·2	„
0·77	99·63	+16·8	„

For the graphic representation of these numbers see fig. 2.

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[*] The salicylate of aniline has not, I believe, been previously described. It is obtained by mixing an alcoholic solution of aniline with the acid. It fuses at about 150°, and cannot be distilled without decomposition. It is slightly soluble in bisulphide of carbon; soluble in ether, hot or cold; soluble in alcohol, hot or cold; soluble in hot benzol, very sparingly in cold.

§ 248. *Pyrogallate of Aniline**.—3·7270 grams of the solution saturated at 17°·8 yielded 1·7440 gram dry salt *in vacuo*, or 46·80 per cent. Of a solution saturated at 0° C., 5·92 grams gave 1·992 gram of the dry salt, or 33·65 per cent. As a cryogen the temperature −4°·6 was obtained, and the cryohydrate showed the same temperature. 9·397 grams of cryohydrate gave 2·253 of salt, or 23·98 per cent. The above results, and the separation of solid matter on loss of heat, are exhibited in the following table:—

TABLE LV.

Per cent. of pyrogallate of aniline by weight.	Per cent. of water by weight.	Temperature at which solidification begins.	Nature of solid.
9·09	90·91	− 1°·0	Ice.
20·00	80·00	− 2·7	„
23·98	76·02	− 4·6	Cryohydrate.
33·65	66·35	0	Salt.
46·00	54·00	+17·8	„

The curve corresponding to these numbers is found in fig. 2. It is to be noted that amongst all the curves referring to the aniline salts, that belonging to the nitrate alone has a well-marked concavity on its ascending branch (from the cryohydrate to the right) turned towards the axis of strength. The very important signification of this curvature will form the key to much in the next Chapter referring to the limit of solubility, or rather to the unlimited solubility in certain cases of certain salts, especially nitrates.

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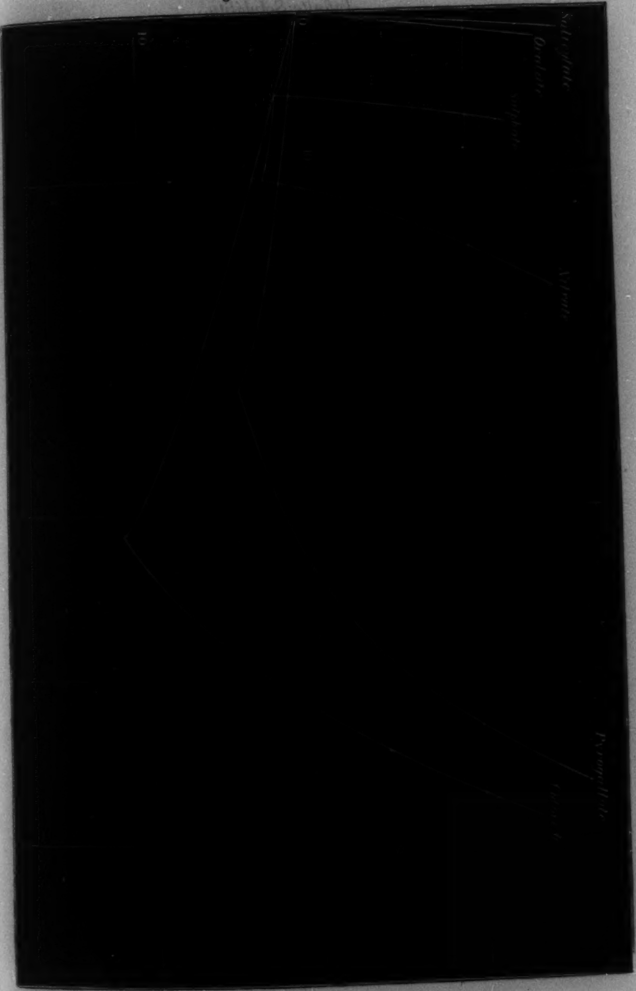
* As I do not find any account of this body, I may briefly note its preparation and properties. On mixing the two substances pyrogallic acid and aniline, a dry hard mass is obtained. As this is soluble in aniline, only a slight excess of the latter is used. The solid mass is dissolved in a minimum of hot benzol; cooled to about 5°, filtered, and washed with cold benzol. Amongst its properties are the following:—It fuses at 126° C. or 128° C. It is very soluble in water, hot and cold; also in hot and cold alcohol and ether; soluble in hot benzol, very sparingly in cold; very sparingly soluble in bisulphide of carbon, hot or cold. Fused on glass, it forms a beautiful crystalline film, the crystals being several inches long. It is anhydrous. In another preparation, 1 part of pyrogallic acid was dissolved in 4 parts of water at 50°. Aniline was added until a specimen became cloudy on cooling. It was cooled to about 10° and filtered through wet paper. It was then evaporated to about half its bulk and dried *in vacuo* over sulphuric acid. It turns brown on exposure to the air.

Fig. 2.—Aniline Salts.



Infinite Solubility.

§ 249. An examination of curves of solubility of salts in water, drawn so that the ordinates are temperatures and the abscissæ are percentages, reveals two types of curves, which differ only essentially in their right-hand or salt-saturated branches. Iodide and bromide and, perhaps, chloride of sodium may be taken as the type of *a*, fig. 3, and nitre of *b*, fig. 3 (see § 126). The curvature of the right-hand branches of both curves must diminish as we travel from the cryohydrate in the direction of the arrows, otherwise there would be two temperatures at which there is the same solubility (*a*, fig. 3, dotted lines) for every solubility between certain limits; or (*b*, fig. 3, dotted lines) there would be two solubilities for every temperature between certain limits. If we concede the impossibility of these conditions, there appear to be three alternatives—the curve loses curvature either parabolically or hyperbolically, or there must be contrariflexure. The first would carry the conditions into the region of critical state and decomposition. The second might mean, in the case of *a* type, if such asymptote be also parallel to the ordinates, that a certain per cent ratio of salt is soluble in water at a certain temperature, and at all higher temperatures; in the case of *b*

Fig. 3.

Cryoh
Cryoh

type, if such asymptote be parallel to the abscissæ, that at a certain temperature a finite mass of water will dissolve an infinite mass of salt.

For the experimental examination of this curious question the salt-alloy of nitrate of lead and nitrate of potash, described in § 215, is excellently well adapted. Its composition is 46·86 nitrate of lead + 53·14 nitrate of potash, and its fusing-point, being 207°, is well within the range of the mercurial thermometer. Its constituents at this temperature are far below their temperature of decomposition, and, what is of equal importance, both the nitrates are essentially anhydrous at all temperatures above 0° C.

§ 250. *a* grams of this salt-alloy, finely powdered and freed from condensed moisture, were introduced into a weighed tube. A little water being then introduced through a capillary tube, the end was sealed off, and both reweighed, the amount of water introduced being thus known. The sealed tube was wrapped round in two places with copper wire, and placed in a copper oil-bath. The bath was heated till complete fusion was effected, the water and salt completely mixing to a colourless limpid liquid. The wire enables the tube to be taken out and the contents moved to and fro.

When complete fusion is obtained the bath is allowed to cool slowly, being kept well stirred. The temperature of incipient solidification is observed several times, to avoid possible errors arising from supersaturation, although with this salt-alloy no such condition appears to obtain. As considerable pressure may be exerted on the tube, it and the thermometer were viewed through two sheets of glass six inches apart. None of the tubes, however have burst.

The following results were obtained:—

Percentage of Salt.	Solidifying temperature.
100	207°
99·82	203° or 204°
98·24	197°

§ 251. These results are striking and important. The phenomenon of fusion *per se* is continuous with, and nothing more than an extreme case of, liquefaction by solution. When we are considering such a case as the second, near the top, where 0·18 weight of water dissolves 99·82 of salt, we are induced to regard it as a solution of water in the fused salt rather than the converse, especially as the solidifying-point is so near that of the dry salt. It will be readily granted that a proportion of the alloy and water having even less water than the above will have an incipient solidifying temperature even closer to the temperature of fusion of the dry alloy. Hence the question, Is this a case of fusion or solution? is to be answered by the reply, It is continuous with both.

The above results with this salt-alloy gave encouragement for the examination of nitre alone with water. The thermal relationship of nitre and water from −3° C., the melting-point of the cryohydrate, to the boiling-point of a saturated solution at one atmospheric pressure, about 115° C., has been pretty fully examined by others and myself. The results are shown in Table LVI. The first sixteen are from my memoir IV., § 129; the next five are on the authority of Gay-Lussac; the last seven, which are those to which I wish here to direct particular attention, are obtained by the use of sealed tubes as described in § 240. The result corresponding to T = 115° is interpolated for the sake of verification from Table LVII. § 253, where a different method of experimenting was undertaken for a different purpose. For T = 100° C., the solution saturated at 114° C. was allowed to cool for several hours in a tube surrounded by boiling water (16·05 grams gave 11·485 grams nitre). For T = 109° C., the solution saturated at 114° C. was allowed to cool for several hours in a tube surrounded by a boiling saturated solution of chloride of sodium (17·83 grams of the solution gave 13·2945 grams of nitre).

§ 252. It must not be overlooked that, although the tubes in the last seven experiments were filled as full of the nitre as the exigencies of manipulation permitted, a certain air-space was unavoidably left into which the water in the tube was free to evaporate. In the last one, indeed, in which water was present its actual weight was only 0·114 gram. This, heated by itself in the free space to 300° C., would have become dry superheated steam. But the fact that it lowered the temperature of solidification 20° C. shows that in the presence of nitre it is not all free. The vapour-tensions of strong solutions of nitre will have to be determined. Correlation with this table or with Wüllner's results is all the more necessary, because, as has been shown by Sorby and others, variation in pressure is not without influence on solubility as well as upon fusion, *per se*.

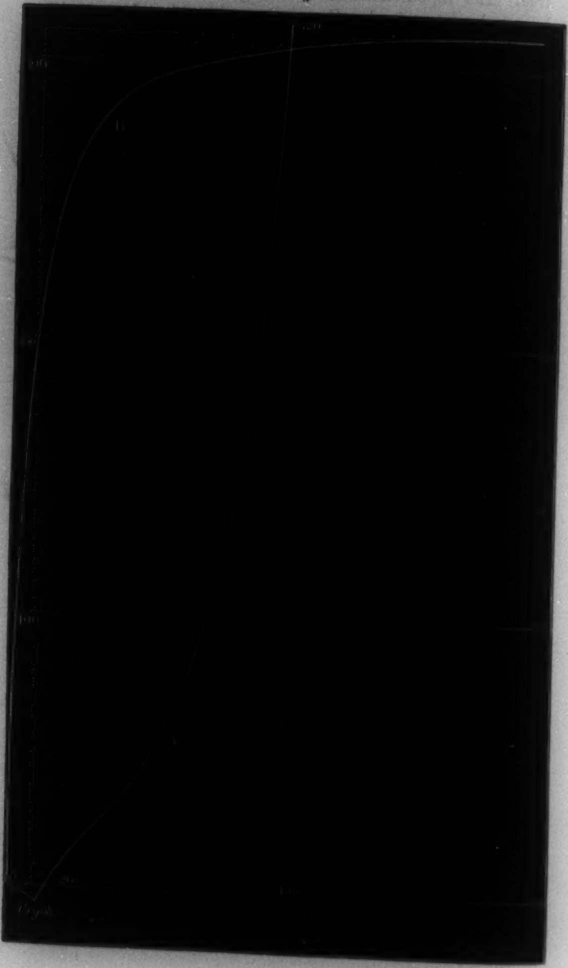
TABLE LVI.

I.	II.	III.	
A solution of nitre in water containing the following percentage of nitre,	that is, to 1 weight of water containing the following weights of nitre,	begins to solidify at the following temperature C.,	giving up as a solid the following:—
0	0·0000	0·0	Ice.
1	0·0101	−0·1	"
2	0·0203	−0·3	"
3	0·0309	−0·7	"
4	0·0417	−1·1	"
5	0·0526	−1·5	"
7	0·0753	−2·2	"
8·5	0·0929	−2·6	"
10	0·1111	−2·9	"
11·2	0·1261	−3·0	Cryohydrate.
12	0·1364	0·0	Nitre.
13	0·1481	+2·0	"
15	0·1765	+6·0	"
20	0·2500	+14·0	"
25	0·3333	+21·0	"
35	0·5385	+35·0	"
40	0·6667	+41·0	"
*43·3	0·7637	+45·1	"
*49·2	0·9685	+54·7	"
*55·4	1·2421	+65·4	"
*62·5	1·6667	+79·7	"
*70·3	2·3663	+97·6	"
71·56	2·5162	+100·0	"
74·56	2·9308	+109·0	"
74·97	2·9956	+114·0	"
75·2	3·0323	+115·0	"
79·14	3·7939	+123·0	"
84·67	5·5231	+151·0	"
89·94	8·9404	+201·0	"
95·11	19·4499	+262·0	"
98·86	86·7193	+300·0	"
100·00	∞	+320·0	"

* Gay-Lussac.

The graphic representation of this relationship is shown in fig. 4, curve A, an ordinate of 1° C. being taken equal to an abscissa of 1 per cent. of nitre. The curve, after dipping to the

Fig. 4.



cryohydrate, rises through 0° C. and reaches the 100 per cent. at 320° C. Perhaps curve B shows the relationship better. It is traced from columns II. and III. It is asymptotic to the temperature-line 320° C., and shows how fused nitre and fused ice are miscible with one another in all proportions.

§ 253. *Boiling-Points of Solutions of Nitre.*—To determine the boiling-points of solutions of nitre of various strengths, 40 grams, which were in the later experiments made up to 100 grams, were placed in a clean tin vessel having a narrow neck, together with a thermometer and an indefinite amount of water. The whole was supported in a hot-air chamber so that the neck only of the tin vessel projected. An arrangement was also made for blowing hot air through the upper part of the vessel. By this arrangement it was hoped that the amount of water condensed in the vessel above the liquid would be inconsiderable. The liquid was boiled until a certain temperature was reached. The vessel was then removed, partially cooled, and weighed. This was done at every half-degree. In the table the temperatures are deduced at which boiling occurs in strengths rising 5 per cent. from 20 per cent. In column II. the results are smoothed out under the assumption that there is a rise of 1°·211 for every 5 per cent.

TABLE LVII.

Per cent.	I.	II.
20	101°·50	101°·50
25	102·83	102·72
30	103·41	103·93
35	104·02	105·14
40	104·50	106·35
45	106·56	107·56
50	107·22	108·77
55	108·85	109·98
60	110·16	111·19
65	110·81	112·40
70	113·00	113·51
75	114·92	114·92

The last of them is saturated at ·758 millim. atmospheric pressure, and the result is inserted in the table, § 252.

§ 254. When a conception such as the above is once fairly grasped, numerous exemplary phenomena which have hitherto been vaguely entertained re-present themselves and claim kindred with it. Thus it is well known that the temperatures of fusion of many organic solids are notably lowered when in contact with water, or even when imperfectly dried; and this is more marked with those whose temperatures of fusion are not high, and which are nominally classed among insoluble bodies. Such bodies will, especially when in a state of fine division, condense water from the air, and hold it with such tenacity that they will not relinquish it wholly and immediately when heated to or even above 100° C. Again, acetate of potassium in solution and subjected to heat, shows continuity of the liquid condition between strong solution and anhydrous fusion. Further, if nitrate of ammonium be dried before a brisk fire, or *in vacuo* over sulphuric acid, it has no associated water. But a solution of that salt in water passes, on evaporation over the flame, from the state of solution to that of fusion without intermediate solidification. Nay, under such treatment it may begin to decompose before it has become anhydrous. This has, indeed, led some experimenters to conclude that in the dry crystalline state it contains a molecule of water. This has arisen from the two facts—first, that it is hygroscopic in moist air, and, second, that one of the products of its decomposition in the dry state is water. The lowering of the boiling-point of a liquid by admixture with even a very little of another liquid having even a higher boiling-point is a phenomenon of the same order.

§ 255. *Geological bearing of* §§ 249–254.—Just as in the selective formation of what in my last memoir were described as salt-alloys we may have the artificial type of the genesis of many primary rocks and metamorphic modifications, so in the wonderful solubility in or miscibility with water of such alloys and of some salts at high temperatures we may have a no less clear type of the formation of certain volcanic rocks and an explanation of some of their peculiarities. The function of water in affecting rocks has been subjected to a most exhaustive examination by Daubrée. Water, in both its solid and liquid form, is a rock. Under pressure the limit of temperature is not known to which it may be heated without decomposition, when in contact with bodies saturated with oxygen. Granting that water may have a so-called critical temperature, and range above it when it is heated with bodies which have no physical relationship towards it, still at high pressures it will be compressible as a vapour to a density at least as great as that of liquid water; and until actual decomposition ensues the physical relationship of the water-molecule with the rock-molecule will remain possibly unchanged. It is true that at the very highest temperatures water appeared to be decomposed; but this is only when it is unconfined.

Whether the earth's temperature be vastly greater towards its centre than it is near the surface, or whether the observed increase with depth be confined to a mere skin of the earth, there seems to be no reason to suppose that water may not, and does not, exist at the earth's very centre.

If the earth were a sphere of liquid having a density of 5, the pressure at its centre would be over three million atmospheres—a pressure competent to preserve the density of water at a temperature sufficient to fuse perhaps the most refractory known rocks. But at this high temperature the water would, judging by analogy, mix freely with the rock and relieve itself—one cannot yet say how much (compare, however, my next memoir, IX.), but certainly very greatly from its tension.

That there are true sedimentary formations of course no one can deny; but to attribute to marine influence the formation of rocks because water is found within them, or because water is liberated when melted rock-masses are ejected, is a contention no longer supportable. Obsidian melted and under pressure will, I presume, mix freely with water. When this pressure is gradually removed, water-vapour escapes, and although it takes with it a large amount of heat, the temperature of the obsidian may still remain above its point of anhydrous fusion, or it may be maintained fused by heat from other sources. Finally cooled, it is the familiar glassy amorphous mineral. A quick release of pressure entails a quick vaporization of water and a quick loss of heat. The obsidian mass, during and because of the loss of water and the loss of heat, becomes pasty and "rises" like dough during fermentation, and becomes pumice, which is often found overlying obsidian. A quicker release of pressure from above causes the vesicular and vesiculating masses to be projected, and if the vesiculation is carried far and fast volcanic dust is produced. That water is one of the accompaniments of volcanic activity is well known. The presence of hydrochloric acid in the ejecta, and the almost universal neighbourhood of the sea to active volcanoes, has favoured the view that the material for the motive power is supplied by the marine irruption. Without entering upon the question as to whether sea-water is essential to volcanoes, and whether hydrochloric acid is a product of the action of acid silicates or silicic acid upon the chlorides in that liquid, I contend that the evidence is conclusive that at one period the melting masses contain water. They are in the same predicament as the nitre liquified along with water at a high temperature and under corresponding great pressure.

This subject has been so fully discussed by Daubrée in his various memoirs, and is so ably treated in his *Géologie Expérimentale*, that, as far as their geological bearing is concerned, my experiments may be considered as merely adding another chapter to his work.

Graham has shown how alumina, silica, oxide of tin, and oxide of iron may be obtained in aqueous solution in the colloidal state; and Daubrée has proved that at high temperature and under pressure water disintegrates and decomposes certain rocks, and rearranges their constituents, and has argued that, assisted by capillarity and high temperature, many phenomena of volcanism and metamorphism are to be attributed to that agent. He has thus vastly extended the scope of the long-known action of water on silicates, and showed that under conditions of temperature water alone plays as potent a part in such disintegration as the fixed alkalies were known to do under like conditions. My experiments may perhaps be considered as leading us a step further. For they show that water at a high temperature may not only play the part of a solvent in the ordinary restricted sense, but that there is in many cases no limit to its solvent faculty; in other words, that it may be miscible with certain rocks in all proportions: that solution and mixture are continuous with one another. And this continuity, as my experiments prove, is established in some cases,—and these indeed with bodies having no chemical affinity with water,—at temperatures not above the temperatures of fusion of those bodies *per se.* This induces me to think that the replenishment of water in rocks by capillarity, an action upon which Daubrée lays great stress and with regard to which he adduces many striking experiments, is not an essential condition. I must, however, leave the discussion of this question to petrologists.

[NOTE *added June* 16, 1884.—Since the above was in print I have been favoured with a copy of a most interesting memoir by Prof. Tilden and Mr. W. A. Shenstone on the "Solubility of Salts in Water at High Temperatures," read before the Royal Society of London, June 21, 1883 (Transactions of the Royal Society, Part I. 1884). Accordingly, wherever in the two memoirs there may be found similarity in results or ideas, the priority is theirs.

These gentlemen have apparently been to a considerable extent guided by the conception that there is a relationship between the solubility of a salt in water and its temperature of fusion. And perhaps their main argument concerns this relationship. They have made a special study of those interesting cases in which the solid salt contains water of crystallization. This branch of the inquiry I have rather deliberately avoided, as I wished to establish the analogy between metallic and dry-salt alloyage, on the one hand, and water-salt alloyage on the other. Nevertheless they examined the solubility of nitre in water at 125°. Their experiments on solubility appear to stop short far below the temperature of fusion of the salt *per se* (excepting in cases where the salt contains water of crystallization). They distinctly state, however, that infinite solubility is "nearly true of benzoic acid, which melts at 120°. . . . . . By sealing it up with water in a glass tube and heating to a few degrees beyond the melting-point, intermixture occurs in all proportions ; and the liquid so obtained, on cooling to 120°, or about 1° lower, becomes turbid from deposition of oily drops, which, however, immediately crystallize."
—F. G.]

XV. *On a new Apparatus for Colour-Combinations. By* H. H. Hoffert, *B.Sc., A.R.S.M., Assistant in the Physical Laboratory, South Kensington**.

[Plate XI.]

Various arrangements for the mixture of colours have already been devised by Maxwell, Rayleigh, Helmholtz, and others, by means of which the laws of colour-combinations have, in their main features, been firmly established.

Wishing to observe for myself the principal phenomena connected with this subject, I have repeated, during the past winter, many of the experiments thus described, both with the colour-top and with overlapping spectra. Being desirous of obtaining some convenient arrangement whereby any two or three colours of the spectrum could be combined in any required proportion, and compared with the colours either of natural objects or of other spectral combinations, I tried various experiments, using the method first adopted by Maxwell, of observing, by means of a slit-eyepiece, the spectra produced by light proceeding from illuminated slits, and passing through a train of glass prisms; this method being equivalent to looking through a hole in a screen on to which are cast two or three superposed spectra, so that the colour perceived is that due to the mixture of those parts of the several spectra which fall on the hole.

In these experiments I have been assisted by my colleague Mr. Mitchell, to whom I am also indebted for several valuable suggestions.

We first tried a modified form of Maxwell's colour-box, using eventually six equilateral glass prisms, arranged in two sets of three symmetrically with respect to the eyepiece; so that if the latter be made a source of light, the rays are bent through about 150°, and being then received on to a lens, are focused on to planes situated on either side of the eyepiece, this arrangement being found very convenient for manipulation.

Movable slits of fixed width, sliding in a frame with bellows-screens of opaque silk between, were used as sources of light,

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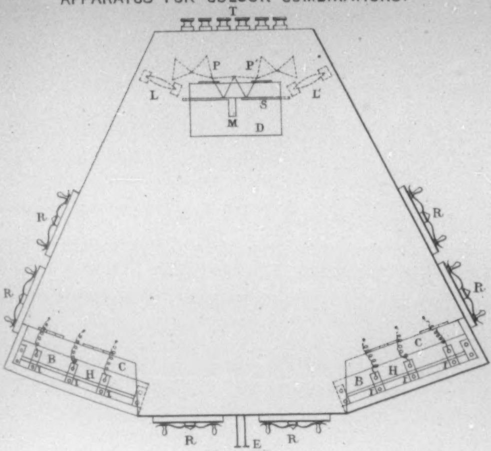
* Read June 14, 1884.

APPARATUS FOR COLOUR COMBINATIONS.


T
P
P'
L
L'
S
M
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R
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R
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C
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C
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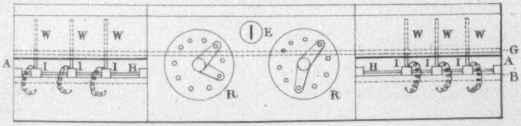
E
R

Plan of Box


W W W
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W W W
G
A
I I I H
H I I I
A
B
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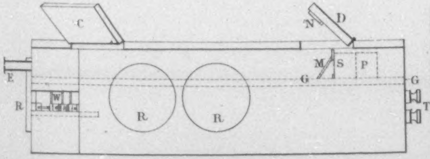
R

Front Elevation of Box.


C
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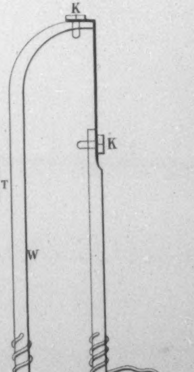
Side Elevation.

Scale 1/8.



Sliding frame carrying the incandescent wire. _ Full size.

Mintern Bros. lith.

lamps being placed outside them. The intensity of the light was regulated by means of Nicol prisms, one being attached to each slit, so as to be capable of rotation, while an analyzing Nicol was fixed in the eyepiece. The intensity could thus be readily altered for each slit separately.

This arrangement was found to answer fairly well, but its necessarily large dimensions were a great inconvenience. A very long spectrum was needed, as the slits could not be brought very close on account of the size of the Nicol prisms; hence also there was great loss of light.

Movable slits, whether of fixed or adjustable width, are very troublesome to manipulate, and do not admit of very rapid and easy adjustment; they were therefore abandoned altogether, and in their place the light from small lengths of platinum wire, heated to incandescence by an electric current, was employed. Preliminary trials having proved satisfactory, the apparatus was constructed which I now bring before your notice.

The prisms, lenses, and sources of light are enclosed in a flat box of irregular hexagonal shape, at the smaller end of which the six prisms (P, Pl. XI.) are placed. These are arranged, as already described, in two sets of three, each prism being set to minimum deviation. The first prisms have their refracting-edges in contact; and by means of a screen (S), in which is a small rectangular aperture, small equal strips of the adjacent faces of these prisms are visible from the eyepiece (E), which is a small brass tube with a narrow slit, about $\frac{1}{16}$ inch wide.

Supposing light to come from the eyepiece, the prisms would deflect it through about 150°; it would then fall on to two lenses (L), of about 10 inches focal length, which focus the spectra on to the two sides of the box immediately to the right and left of the eyepiece. Here are placed the incandescent wires (W); so that, conversely, if these be the sources of light, the rays follow an inverse course, and the corresponding half of the aperture in the screen is seen illuminated with a colour which will depend on the position of the incandescent wire, and which will be pure and uniform if the wire be not too thick, the slit in the eyepiece too wide, or the strip of the prism exposed too large. The colours are found in practice to be perfectly uniform.

The prisms and lenses are supported at the level of the incandescent wires, on a horizontal floor (G), which divides the box two inches from the top into two compartments, and which is cut away so as to leave a space for the tops of the frames carrying the wires to enter the upper compartment. These frames (W), which are six in number, three on each side, consist of brass wires held on small ebonite blocks (I), which slide along a steel rod (H) supported on a ledge inside the box. The frames can be moved along the length of the spectrum from outside by means of openings (A) cut in the sides of the box, into which the hands can be introduced. These openings are below the level of the horizontal floor, so that the upper compartment, which is everywhere blackened inside, is quite impervious to external light, unless the lids in the cover of the box, to be presently described, are opened.

The frames are connected by flexible wires to a series of resistances arranged in the lower compartment of the box; and by means of six dials (R), on the sides of the box, each of the six circuits can be altered in resistance at will, so that the incandescent wires can be rapidly adjusted, whether in position or in intensity, by the observer without his having to remove his eye from the eyepiece. Six pairs of binding-screws (T) at the back of the box connect the six circuits with a Grove battery. By this means, when the current is passing, the aperture in the screen is seen divided into two coloured strips in close juxtaposition; one colour being that due to the wires and prisms on the right hand, the other to those on the left. The colours can thus be readily compared and adjusted to exact identity.

It remains to describe the means by which external colours can be introduced for comparison with those produced by the prisms.

The cover of the box contains three small hinged lids. Two of these (C) are over the luminous wires, and serve to adjust or replace the wires in case of accidental fusion. The third lid (D) opens over the space just in front of the screen. Here is placed a small strip of microscope cover-glass (M), inclined at about 60° to the horizontal, and so arranged that, as seen from the eyepiece, it exactly covers that portion of the aperture in the screen which is illuminated by the light from the left-hand train of prisms, this light being thus seen through the glass slightly diminished in intensity. On the underside of the lid is a small silvered mirror (N); and by raising the lid to the proper height, the colour of any object laid on the top of the box is seen by double reflection in the eyepiece, exactly coinciding with the left half of the aperture in the screen. This colour may be either combined with that from the left-hand train of prisms, or compared with that from the right-hand train. For white light I use the light from a window, which may be reduced in intensity to any desired amount by passing it through one or more pieces of roughened glass, held in a frame placed on the top of the box. Coloured glasses, or cells of coloured fluids, can similarly be placed in the frame, so that almost every possible combination or comparison of colours may be made. Another frame, which may be placed inside the box between the screen and the eyepiece, serves to show the action of different absorbing media on colours identical in appearance but of different composition.

The colours produced are uniform, very constant, and fairly bright. Those from the blue and violet parts of the spectrum are necessarily more deficient in luminosity. This is partially compensated by using in the less luminous parts of the spectrum ribbons of platinum, produced by rolling out the wires, with their flat surfaces turned towards the lenses. This is equivalent to increasing the width of the slit in ordinary arrangements. Should the wires become fused through incautiously using too strong a current, they can be very readily replaced by means of the screws (K).

For the current, three Grove's cells are needed for each of the ribbons and two for each of the wires. But since the frames carrying the wires can be brought together till the wires are nearly in contact, and since the wires themselves offer extremely narrow luminous surfaces, a very long spectrum is not needed; and by using more powerful lenses and bringing the sliding frames closer to them, a greater intensity of light would result; while the size of the box might thus be reduced to one half or even less of its present amount, the eyepiece being kept at a sufficient distance by the use of a longer tube, which might be made removable. One Grove cell would then suffice for each wire, or at most two when experimenting on the violet rays.

Instead of the step-by-step dial-resistances, some arrangement giving, like the rheostat, a gradual adjustment of the intensity would be perhaps preferable.

Scales can be attached in front of the sliding frames to show the exact position in the spectrum of each of the luminous wires.

I trust that the ease and rapidity with which the adjustments in this apparatus can be made will cause it to be found useful in those many cases in which it is impossible or inconvenient to make use of the more powerful effect of direct sunlight.

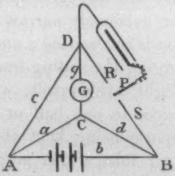
XVI. *On a Method of Measuring the Electrical Capacity of a Condenser, and on the Determination by Electrical Observations of the Period of a Tuning-fork.* *By* R. T. GLAZEBROOK, *M.A., F.R.S., Demonstrator of Experimental Physics at the Cavendish Laboratory, Cambridge**.

THE experiments described in the following paper were undertaken at the request of Messrs. Latimer Clark, Muirhead, and Co., for the purpose of testing one of their condensers "which," quoting from a letter from the firm, "has lately been made and which we use in the factory. In its construction it is the same as all our condensers, and is made of sheets of mica and tinfoil and laid with paraffin-wax."

The method employed was a modification of one given by Maxwell (vol. ii. § 776), and used by J. J. Thomson (Phil. Trans. iii. 1883) in his recent determination. The following is his description of the arrangement:—

"In a Wheatstone bridge, A B C D (fig. 1), with the galvanometer at G and the battery between A and B, the circuit B D is not closed, but the points B and D are connected with two poles, R and S, of a commutator, between which a travelling piece, P, moves backwards and forwards. P is connected with one plate of a condenser, the other plate of which is connected

Fig. 1.



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* Read June 28, 1884.

with D. Thus, when P is in contact with S the condenser will be charged, and until it is fully charged electricity will flow into it from the battery: this will produce a momentary current through the various arms of the bridge. When the moving piece P is in contact with R, the two plates of the condenser are connected, and the condenser will discharge itself through D R; and as the resistance of D R is infinitesimal in comparison with the resistance in any other circuit, the discharge of the condenser will not send an appreciable amount of electricity through the galvanometer. Thus, if we make the moving piece P oscillate quickly from R to S, there will, owing to the flow of electricity to the condenser, be a succession of momentary currents through the galvanometer. The resistances are so adjusted that the deflection of the galvanometer produced by these momentary currents is balanced by the deflection due to the steady current, and the resultant deflection is zero. When this is the case, there is a relation between the capacity of the condenser, the number of times the condenser is charged and discharged in a second, and the resistances in the various arms of the bridge."

The investigation given by Maxwell is only approximate; we shall quote therefore the result given in Thomson's paper.

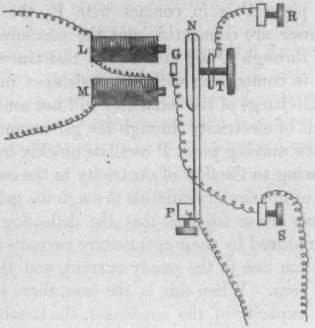
Let a be the resistance of A C,
b ,, ,, A B,
c ,, ,, A D,
d ,, ,, B C,
g ,, ,, D C.

Let C be the capacity of the condenser, n the number of times it is charged and discharged per second; then

$$nC = \frac{a\left\{1 - \dfrac{a^2}{(a+c+g)(a+b+d)}\right\}}{cd\left\{1 + \dfrac{ab}{c(a+b+d)}\right\}\left\{1 + \dfrac{ag}{d(a+c+g)}\right\}}.$$

The commutator was the one used by J. J. Thomson, and we will quote his description:—"The current from some Grove cells passes first through a tuning-fork interrupter and then through the coils L M (fig. 2) of an electromagnet. P N is a strip of brass with a piece of iron wire attached to it

Fig. 2.



When there is no current passing through the electromagnet the elasticity of the rod P N makes it press against the screw T, which is electrically connected with the binding-screw R. When the current passes through the electromagnet, the magnet attracts the iron attached to the rod P N and brings it into connexion with the stop G, which is electrically connected with the binding-screw S. The letters P R S indicate the same points in this figure as in fig. 1. All the places where contact is made are covered with platinum, and the whole arrangement is fastened down to an ebonite board. As the current passes intermittently through the coils L M of the electromagnet, the vibrating-piece P N strikes alternately against the parts G and T. When it strikes against G, the opposite plates of the condenser are connected with the two poles of the battery; when it strikes against T, the condenser is discharged."

The main advantages of this method over the one ordinarily employed for the determination of the capacity of a condenser whose capacity is comparable with a microfarad are easily seen. In the first place it is a null method; no assumptions are required as to the constancy of the battery. In the second, the galvanometer can readily be made much more sensitive. For accurate work in the ordinary method, the field of force in which the galvanometer-needle hangs should be nearly uniform. The earth's force is much too strong, unless an enormous battery-power be employed, and it is difficult to secure a uniform field by a control magnet. Something may of course be done by the use of an astatic galvanometer-needle; but it is impossible to increase the sensitiveness in this way very much, because the torsion of the suspending fibre then becomes important. Again, in the ordinary method the time of swing cannot be determined accurately if it be made too small; the moment of inertia of the suspended parts therefore must be considerable, and the deflection produced by a given quantity of electricity suddenly discharged through the galvanometer is proportionately decreased; for, if T be the time of swing, θ the throw produced by a quantity of electricity Q, then $T \sin \frac{1}{2} \theta$ is proportional to Q. In addition to this, there is the correction for damping which has to be considered.

On the other hand, objections may be raised to the method which has just been described. The most important of these is founded on the fact that the time during which the plates of the condenser are in contact either with each other or with the poles of the battery is very short. It may happen, then, that the condenser is neither charged nor discharged completely at each vibration of the commutator; while if there be any electrical absorption in the condenser, its effects will depend on the time during which the contact lasts. The experiments to be described were undertaken with the view of testing the method for these defects. The time during which the plates of the condensers are connected with the battery is the time during which the spring P N is in contact with G. This is only a fraction of the period of the tuning-fork which governs the commutator, a fraction which depends on the distance between the end of the screw T and the point G, and on the strength of the current in the electromagnet.

A series of experiments were made to test the effect of varying the position of the screw T, keeping the battery the same. In these, four Leclanché cells were used in the battery-circuit A B, and two pint Groves to drive the commutator.

The position of the spot of light on the scale was noted, and then the value of the resistance *d* adjusted until no deflection was produced when the galvanometer-circuit was closed by means of a key.

The commutator, when working correctly, emitted a definite sound which was readily recognized; and it was found that the screw T could be adjusted within certain limits without altering this sound.

Table I. gives the results of these observations.

TABLE I.

Commutator adjustments.	Value *d* in B.A. units.
Screw T set	905
Screw T readjusted, note good	906
" " " "	906
" " " bad	906
" " " good	906
Screw T loosened one turn. Spot off scale.	
Screw T readjusted, note good	906

Thus the value of *d* required to give a balance is practically the same throughout, and the commutator with a definite battery-power can readily be set to give a definite result; moreover, a balance could never be obtained except with the resistance 905 or 906. In the fourth observation the note of the commutator was marked as bad; but the spot remained stationary, showing that though there seemed to be a slight irregularity in the sound, it was too small to affect the balance. The sensitiveness was such that an alteration in *d* of 1 B.A. unit produced a deflection of from two to three scale-divisions. The number of vibrations of the fork was about 32 per second.

Another set of observations was then taken to test the effect of varying the battery-power driving the commutator, thus altering the force with which the spring P N is attracted to G, three Grove cells being used in place of two. The values of *d* found in two separate observations were 905·5 and 905.

Observations were made to test the effect of varying the period of the driving-fork. Forks of frequencies of approximately 16, 32, 64, and 128 to the second were taken, and the pitch of the lowest of these determined absolutely by comparison with the clock in the method described by Lord Rayleigh ('Nature,' xvii. p. 12; Phil. Trans. 1883, Pt. I.). This fork and the 32 fork were then set going on independent circuits, and a pointer attached to the 32 fork was watched over the top of a plate of thin metal which had been all along fixed on to the 16 fork, the eye being placed so that this pointer was visible for only one position of the 16 fork in each vibration. In this way the beats between the octave of the 16 fork and the 32 fork were visible, and could easily be counted.

Thus the period of the 32 fork was found, and then in a similar manner those of the 64 and 128 forks. By loading with wax one of the two forks under comparison, it was easy to find which of the two was gaining.

Each of these forks was used in turn to drive the commutator, and the value of the capacity calculated from the observations. The values of the resistances were as follows:—

a was a standard coil of 10 B.A. units, *d* a resistance of 1000 B.A. units, taken from a box by Messrs. Elliott, Bros., and *c* a variable resistance from another box by the same firm.

g, the galvanometer-resistance, was about 11,000 B.A. units; and *b*, the battery-resistance, from 5 to 6 B.A. units. The galvanometer-resistance was higher than necessary, but it was for other reasons the most convenient instrument for the purpose. The value of *c* varied from about 1800 to about 240 B.A. units.

It will be found that, with these values, the equation giving the capacity may be written

$$nC=\frac{a}{cd\left\{1+\dfrac{a}{d\left(1+\dfrac{c}{g}\right)}\right\}}.$$

[The approximate equation given in Maxwell is

$$nC=\frac{a}{cd}.]$$

We shall use N_{16} &c. to denote the frequency of the fork of approximate frequency 16.

The following are the results of the observations:—

(1) Fork 16 used.

Fork compared with pendulum. Fork loses 1 vibration in 7·46 seconds.

$$N_{16}=15{\cdot}866 \text{ sec.}$$

Resistance observation:—

$$a=10;\quad d=1000;\quad c=\left\{\begin{matrix}1895\\1892\\1893\end{matrix}\right\}1893 \text{ mean.}$$

Sensitiveness 1 scale-division for alteration of 1 B.A. unit in c.

From these we find

$$C_{16}=\cdot 3300\,\frac{\text{ohm}}{\text{B.A. unit}} \text{ microfarad.}$$

(2) Fork 32 used.

16 beats occur in 42 seconds between octave of 16 and 32. Fork 32 gaining.

$$N_{32}=32{\cdot}11.$$

Resistance observations:—

$$a=10;\quad d=1000,\quad c=\left\{\begin{matrix}934\\934\\934\end{matrix}\right\}934 \text{ mean.}$$

Hence

$$C_{32}=\cdot 3304\,\frac{\text{ohm}}{\text{B.A. unit}} \text{ microfarad.}$$

(3) Fork 64 used.

10 beats occur between 64 and octave of 32 in 50 seconds. Fork 64 gaining.

$$N_{64}=64{\cdot}42.$$

Resistance observations:—

(α) $a=10;\quad d=1000;\quad c=466;$

$$C_{64}=\cdot 3299\,\frac{\text{ohm}}{\text{B.A. unit}} \text{ microfarad.}$$

(β) $a=10;\quad c=1000;\quad d=\left\{\begin{matrix}461\\461{\cdot}5\end{matrix}\right\}461{\cdot}3 \text{ mean.}$

$$N_{64}=\cdot 3299\,\frac{\text{ohm}}{\text{B.A. unit}} \text{ microfarad.}$$

(4) Fork 128 used.

16 beats occur between the 128 fork and octave of 64 fork in 26·25 seconds. Fork 128 gaining.

$$N_{128}=129{\cdot}05.$$

Resistance observations:—

$$a=10\,;\quad d=1000\,;\quad c=232{\cdot}5.$$

Hence

$$C_{128}={\cdot}3301\,\frac{\text{ohm}}{\text{B.A. unit}}\text{ microfarad.}$$

The sensitiveness throughout these observations was such that an alteration of 1 in 2000 in the resistance produced a deflection of about one scale-division in the spot of light.

Hence the greatest difference in the observations amounts to about 5 in 3300, or about 1 in 660; and there is no trace visible of variation in the capacity with the time of charging.

We will collect the numbers together:—

C_{16}	·3300
C_{32}	·3304
C_{64}	·3299
C_{64} (second arrangement)	·3299
C_{128}	·3301

$$\text{Mean value of capacity}={\cdot}33006\,\frac{\text{ohm}}{\text{B.A.U.}}\text{ microfarad.}$$

Taking the Cavendish-Laboratory experiments, we have

$$1\text{ B.A. U.}={\cdot}9867\text{ ohm.}$$

$$\therefore\quad C=\frac{{\cdot}33006}{{\cdot}9867}\text{ microfarad}$$

$$={\cdot}3344\text{ microfarad.}$$

If we take the legal ohm and the value of the specific resistance of mercury in B.A. units, adopted by the B.A. Committee,

$$1\text{ B.A. unit}={\cdot}9889\text{ ohm,}$$

and

$$C={\cdot}3336\text{ microfarad.}$$

This value supposes that the various coils used have their nominal resistance in B.A. units. And this assumption is correct, at any rate to 1 in 1000. Thus it seems that the method gives satisfactory results, and may safely be used to determine the capacity of a condenser.

But the converse of the method may be even more useful. The fundamental equation gives us C if we know n and the resistances; it will equally give us n if we know C and the resistances; and in many cases this may be the readiest method of finding n, especially if the period is too long to give an audible note. Thus in the above experiments I require to adjust a fork to vibrate about 16 times a second, the lowest I could obtain being one of a frequency of almost 20.

I made observations with the 32 fork, the pitch of which was marked on it by the maker, of the value of c required to produce a balance, then doubled this value of c, and set the fork which it was required to adjust to drive the commutator. Leaden weights were then fixed with screws on to the prongs of the fork, and their position was adjusted until the galvanometer-balance was not disturbed on making contact. It was clear, then, from the approximate formula that the frequency of the fork was very nearly 16. And on making the comparison with the clock, it was found to be 15·866, as already stated.

My thanks are due to Messrs. Wilberforce, Whitehead, and Fitzpatrick for assistance in making the experiments.

XVII. *On the Thermal Relationship between Water and certain Salts.* *By* B. Illingworth *and* A. Howard*.

The study of the relationship towards water of certain organic salts belonging to one and the same series promised to throw light upon the general question of the relationship between salts and water, inasmuch as the *degree* of difference between the members compared may be made at will very considerable; while the *kind* of difference is not to be compared with that resulting from the substitution of an acid or basic element in a given salt.

We have accordingly submitted to examination the sulphomethylate, the sulphoethylate, and the sulphoamylate of potassium ($K, CH_3 SO_4$; $K, C_2 H_5 SO_4$; and $K, C_5 H_{11} SO_4$); and we venture to think that the results are of sufficient interest for us to give the following brief account of them.

We satisfied ourselves that the substances were nearly pure. The methyl salt contained, however, a trace of chlorine, and the amyl salt was not quite free from the same impurity. They were finely powdered, and dried over sulphuric acid in partial vacuum until they ceased to lose weight. A thermometer, the error of which at 0° was determined, and which was graduated to tenths of a degree (each tenth being $\frac{8}{10}$ millim. long), enabled us to read temperatures with considerable precision.

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* Read June 14, 1884.

Sulphoethylate of Potassium ($K, C_2 H_5 SO_4$).—Starting with the ethyl salt, a preliminary examination, made by mixing the salt with about twice its weight of finely crushed ice, showed the cryogen value to be $-13°·9$ C. This, according to analogy, should be the melting- and solidifying-temperature of the cryohydrate. Solutions containing various percentages of the anhydrous salt were made and submitted to a salt-ice cryogen, the temperature being noted at which solidification began.

With regard to the solubility at the air-temperature :—A solution saturated at 21° C. was allowed to cool for several hours until it reached 15°·1 C. Of this solution, 7·3342 grams were weighed in a covered basin and then dried *in vacuo* over sulphuric acid. The nearly dry mass was powdered and redried until it ceased to lose weight. 4·5732 grams, or 62·35 per cent., were thus obtained.

A solution saturated at the air-temperature was fairly buried in melting ice for several hours and until its temperature had remained for a few hours at 0° C. Examined as above, 24·0880 grams gave 12·9375 grams of anhydrous salt, or 53·71 per cent.

A solution of strength between 40 and 50 per cent. was cooled in an ice-salt cryogen until its temperature remained constant at $-14°·2$ C. After a considerable amount had solidified, 11·9813 grams of the solution were dried, and yielded 5·3932 grams dry salt, or 45·01 per cent. It will be noted that the temperature of the cryogen of this salt was found to be $-13°·9$, or 0°·3 higher than the melting-point of the cryohydrate.

TABLE of Sulphoethylate of Potassium and Water.

Sulphoethylate of potassium, per cent.	Water. per cent.	Temperature at which solidification begins.	Body separated.
10	90	− 2°·2	Ice.
20	80	− 4·9	"
30	70	− 8·2	"
40	60	−12·1	"
45·01	54·99	−14·2 (cryogen −13°·9)	Cryohydrate.
50	50	− 6 (interpolated)	Salt.
53·71	46·29	0	"
62·35	37·65	+15	"

Sulphomethylate of Potassium $(K, CH_3 SO_4)$.—The mode of procedure was precisely like that above described.

As a cryogen, it showed a temperature of −11°·3.

At the air-temperature (12°·3) an amount of 5·2254 grams gave 2·8654 grams residue, or 54·8 per cent.

16·5250 of the solution saturated at 0° gave 2·8654, or 47·08 per cent.

The solidifying-temperature of the cryohydrate was found to be −11°·8; and 9·4940 grams of it yielded 3·7824, or 39·84 per cent. anhydrous salt.

TABLE of Sulphomethylate of Potassium and Water.

Sulphomethylate of potassium, per cent.	Water, per cent.	Temperature at which solidification begins.	Body separated.
10	90	− 2°·3	Ice.
15	85	− 3·6	"
20	80	− 5·0	"
30	70	− 8·0	"
39·84	60·16	−11·8 (cryogen −11°·3)	Cryohydrate.
40	60	−11·5 (interpolated)	Salt.
47·08	52·92	0·0	"
54·8	45·2	+12·3	"

Sulphoamylate of Potassium $(K, C_5 H_{11} SO_4)$.—This salt *, on being treated in quite a similar manner, gave the following results.

The temperature of the cryogen was found to be −5° C.

At the air-temperature (17°·3), a solution weighing 6·8099 grams gave 4·0494 grams residue, or 59·46 per cent.

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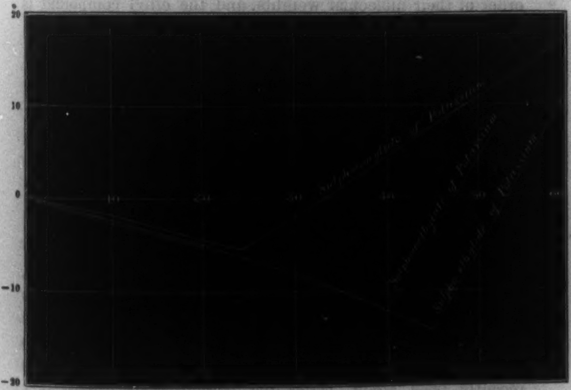
* Probably isoamylate.

The solidifying-temperature of the cryohydrate was found to be −5·4; and 11·958 grams of it gave 2·8737 grams of anhydrous salt, or 24·03 per cent. 15·667 of the solution, saturated at 0°, gave 5·240 of anhydrous salt, or 33·44 per cent.

TABLE of Sulphoamylate of Potassium and Water.

Sulphoamylate of potassium, per cent.	Water, per cent.	Temperature at which solidification begins.	Body separated.
10	90	− 1°·9	Ice.
20	80	− 4·3	,,
24·03	75·97	− 5·4 (cryogen −5°)	Cryohydrate.
25	75	− 4·8 (interpolated)	Salt.
33·44	66·56	0·0	,,
59·46	40·54	+17·3	,,

The accompanying figure shows the relationship, in respect to water, of these three closely allied salts. The abscissæ are percentages, the ordinates temperatures.



The ethyl and methyl combinations run an almost common course as far as the cryohydrate of the latter. They cross at about 24 per cent. The cryohydrate of the ethyl salt contains about 5 per cent. more salt and melts at 2°·4 lower. The ascending or salt branches of the curves are almost absolutely parallel, but exhibiting a slightly opposite curvature.

Perhaps the most salient fact concerning this group is that the methyl compound is intermediate in these of its physical properties between the ethyl and the amyl members. So interesting did this relationship appear, that we have determined the specific gravities of the three salts. Turpentine was used as the liquid displaced. The dry salt having been weighed in the specific-gravity bottle, a little turpentine was added and the air exhausted. The bottle was subsequently filled with turpentine in the usual way. The air-temperature was 19°·6, and the specific gravity of the turpentine compared with water at the same temperature was 0·86838. It was found that

$$\text{at } 19^\circ{\cdot}6 \begin{cases} \text{sp. grav. of sulphomethylate of potassium} = 2{\cdot}097, \\ \quad ,, \quad ,, \quad \text{sulphoethylate of potassium} = 1{\cdot}843, \\ \quad ,, \quad ,, \quad \text{sulphoamylate of potassium} = 1{\cdot}144. \end{cases}$$

Accordingly the densities of the salts are in the inverse order of their molecular weights, and the ethyl compound is in this respect in its usual place between the amyl and methyl relatives.

Physical Laboratory, Science Schools,
South Kensington.

XVIII. *Preliminary Notice of a new Sunshine-Recorder.* *By* Herbert M'Leod, *F.R.S.*[*]

Being somewhat doubtful of the accuracy of the published reports of the duration of sunshine, in the summer of 1880 I tried to devise some apparatus by which the light, instead of the heat of the sun, would be used to produce the record of sunshine. Several trials were made; and in some of them clockwork was employed to move strips of sensitive paper. The simplest form of apparatus I have recently tried again, using the ferroprussiate paper now much employed by engineers for copying tracings, and which is preferable to silver paper, first, in consequence of its cheapness, and, secondly, because of the ease with which the image is fixed, as for this purpose washing in water is sufficient.

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[*] Read June 28, 1884.

The apparatus consists of a camera so fixed that its axis is parallel to the polar axis of the earth, the lens pointing northwards. Opposite the lens a silvered sphere is placed. The rays from the sun are reflected from the sphere through the lens of the camera on to the sensitive paper, on which a distorted image of the sun is formed; and the positions of the lens and sphere are so arranged that the image is a linear one and radial. By the motion of the earth the image is carried round in a circular arc, tracing a curve on the sensitive paper. In the instrument at present constructed, the sphere is a chemical round-bottomed flask silvered inside, and about 95 millim. in diameter; the distance from flask to lens is 76 millim., and from lens to sensitive paper 152 millim.; the lens has a focal length of 90 millim. and an effective aperture of 22 millim.

The circle traced by the sun in June is about 120 millim. in diameter. An impression is made on the paper by exposure for only 10 seconds; and when the lens is covered for one minute, a light line is produced in the circular band, so that the paper is sufficiently sensitive in the present apparatus to register short gleams of sunshine, and also the passage of small clouds. When the sun is shining through light clouds, an impression is produced on the paper, but somewhat blurred, and of a much less intense blue colour than is obtained by bright sunshine. The time-scale is made by drawing from the centre of the circular band radial lines, containing between them angles of 15°, each of which represents one hour of time.

It still remains to be found which are the most convenient dimensions for the globe and lens, so that the minimum of alteration of position will be requisite to obtain a sharp image during all times of the year; and also the best method of fixing the paper so that it may be easily changed and the time-scale marked on it.

XIX. *A Magneto-electric Phenomenon.* *By* C. V. Boys, *A.R.S.M., Demonstrator of Physics at the Science Schools, South Kensington*[*].

Every one is familiar with the effect produced when a copper disk is set to spin in a powerful magnetic field: the currents induced by the motion of the disk act in such a direction as to oppose the motion, which therefore speedily ceases. Faraday observed that if, instead of being set to spin, a disk is merely suspended between the poles of an electromagnet, it will in general be disturbed whenever the current in the coils of the electromagnet is made or broken. If it lie with its plane parallel or at right angles to the lines of force, no disturbance will be apparent if the lines of force where they are included by the disk are parallel. But if the plane of the disk makes an angle α with the parallel lines of force, then on mak ingthe current in the electromagnet an impulse is given tending to diminish the angle α, while breaking the current gives an impulse tending to increase the angle α.

Again, if the angle α be 90°, so as to eliminate this twisting effect, no movement will be visible at the making or the breaking in a parallel field; but if the disk be placed in a field with diverging lines of force, in which, of course, the strength diminishes as the lines separate, and if it be placed symmetrically so as to include the greatest number (*i. e.* with its plane at right angles to those lines passing through its centre), then, on making the current, it will receive an impulse causing it to move parallel to itself along the lines of force towards the weaker part of the field, and at the breaking it will receive an impulse more evident in the opposite direction. If this radiating field is produced between a pointed and a flat pole, the disk will, on making the current, appear to be repelled from, and, on breaking, to be attracted by, the pointed pole. So powerful is this effect that a piece of impure copper, which is strongly magnetic, is repelled from the pointed pole on making, and attracted on breaking, the current, thus appearing at first sight strongly diamagnetic.

Though these impulses must have been observed by most experimentalists, their amount has not been, so far as I am aware, determined in absolute units, nor have they been turned to account for making any measurements. As they seem to afford one of the most convenient methods of determining conductivity and field-intensity, perhaps a short paper on the subject, even though it be incomplete, may be of interest to this Society.

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[*] Read June 28, 1884.

The explanation of the motions described will be obvious, but it may be well to give it at length for the sake of arriving at quantitative results. In the first place, let the lines of force be parallel, so that the field is of uniform strength. Let a ring of (small) section s, of specific resistance ρ, and of radius r, be placed in the field, with its plane making an angle α with the lines of force. Let the strength of the field be H units. Then during a small increment of field-intensity $d\mathrm{H}$, in the time dt, a current will be induced in the ring of the strength

$$\frac{rs\sin\alpha}{2\rho}\,\frac{d\mathrm{H}}{dt}.$$

This current in the field H will produce a twisting tendency to increase α with a diminishing, or to diminish α with an increasing field, represented by the couple

$$-\frac{\pi r^3 s\mathrm{H}\sin 2\alpha}{4\rho}\,\frac{d\mathrm{H}}{dt}.$$

From this it is clear that the couple varies inversely as the time dt occupied in making any small change of field-intensity $d\mathrm{H}$, but it lasts for the time dt; therefore the momentum acquired by the suspended disk, if free to move, will be independent of the rate at which any small change in the magnetic field may be made, but will depend only on its amount, provided that the time is not sufficient for the angle α to have perceptibly altered during the change. Since this is true of any element, it is true of all; so the momentum acquired by the ring is a direct measure of any total change in the strength of the field in which it lies, no matter by what law it changes in strength. If at the end of any rapid change the field remains of any strength, the motion of the ring will be rapidly stopped by the well-known damping action, of which I shall have more to say later. If, however, the field sinks to zero, or nearly so, the momentum acquired can be measured and the original intensity determined.

The current induced in the ring will of course react on the field and bend the lines of force in such a manner as to hinder their passing through its edge, that is to delay the change of included field-intensity; but the impulse is independent of the time or the manner in which the field changes, so it cannot be effected to any extent by this cause.

Since the impulse given to the disk during any element of time is

$$-\frac{\pi r^3 s \mathrm{H} \sin 2\alpha}{4\rho}\,\frac{d\mathrm{H}}{dt},$$

the total impulse while H changes between 0 and H will be

$$-\frac{\pi r^3 s \mathrm{H}^2 \sin 2\alpha}{8\rho}.$$

If the moment of inertia of the disk be M, and the torsional value of the supporting wire be T, the angular velocity ω generated will be

$$\omega = -\frac{\pi r^3 s \mathrm{H}^2 \sin 2\alpha}{8\rho \mathrm{M}},$$

and the throw of the ring θ will be

$$\theta = -\frac{\pi r^3 s \mathrm{H}^2 \sin 2\alpha}{8\rho\sqrt{\mathrm{MT}}}.$$

The action on a disk may be considered as the sum of the actions on the several elementary rings of which it is composed, for there cannot be any tendency for any part of the currents to cross over the elementary circles. The impulse therefore on a disk of radius r and thickness s will be

$$-\frac{\pi r^4 s \mathrm{H}^2 \sin 2\alpha}{32\,\rho};$$

and the impulse on a disk of radius r_2 with a concentric hole of radius r_1 will be

$$-\frac{\pi s \mathrm{H}^2 \sin 2\alpha}{32\,\rho}\,(r_2^4 - r_1^4).$$

Since the moment of inertia of a disk is also proportional to the fourth power and to the thickness, so long as the thickness is small, it will appear that the velocity imparted to a disk of any size or thickness, or to a ring, during a change in a magnetic field will be the same. To what extent a correction should be applied to these results for self-induction between different parts of the disk I am not prepared to say; their calculation would give trouble.

For comparing one field with another, disks or rings of metal may be used; but for absolute measurements, as it would be impossible to measure the exact conductivity of a disk, a coil is preferable. By employing disks of different metals their conductivities can be compared without the trouble of drawing into wire or cutting into long strips.

It will be found that a coil of area A and resistance R will, under a torsion T, experience a throw

$$\theta = -\frac{A^2H^2 \sin 2\alpha}{4R\sqrt{MT}}.$$

If, instead of a disk, a sphere be used, no twisting should be experienced if the conductivity in different directions is the same. If, however, there is a plane of greatest or least conductivity, it should be possible to discover it. Crystallization or mechanical treatment might give rise to such planes in metals; no definite results could be expected in any thing else.

I have referred to the apparent repulsion and attraction of a disk of metal by a pointed pole at the making and breaking of the magnetizing current. As the lines from such a pole radiate outwards, they are not normal to the metal except in the middle. On their passage inwards or outwards they give rise to circular currents tending to move each part of the disk normally to the lines of force. There is therefore a longitudinal component away from the point of radiation during an increase in the field, and towards it during a diminution of the field. A closed coil of wire is subject to the same forces. If a coil be made of uncovered copper wire in the form of a double helix with the ends joined together, and if the convolutions are separate so as nowhere to touch one another, the growth of the magnetic field can be watched by placing the coil nearly over one pole. On making the current the field begins to grow, at first quickly and afterwards more slowly. The coil will receive a push and will extend itself. As the push diminishes in amount, owing to the diminishing rate of growth of the magnetic field, the coil will gradually regain its former shape. It might be thought that the slow recoil is simply due to the damping action of the field; but this is not sufficient to account for it, as when the field is fully grown the coil will, on being forcibly drawn out, recover its shape much more quickly. On breaking the magnetizing current, the impulse in the opposite direction, being the same as before but lasting for so much shorter a time, is far more evident.

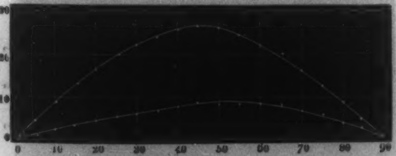
My first experiments were made with a view to determine whether the impulse was proportional to sin 2α when other things remained the same. I therefore cemented a disk of metal (a half-crown) to an ebonite rod carrying a glass index and hung by a torsion-wire of platinum. The glass index travelled over a card divided into degrees; and the wire to which the upper end of the torsion-wire was soldered also carried a pointer, the position of which could, if desired, be read on a divided card. The disk was suspended between two parallel polar faces of iron. The upper index was turned until, on making and breaking the current, the lower index showed no sign of motion. It could thus be placed within a small fraction of a degree, so that α was either 90° or 0°. The lower card was then adjusted, and the upper index turned so that the lower rested successively at 5°, 10°, 15°, &c. up to 90°. The negative impulse on making, and the positive impulse on breaking, the current were observed by the throw of the lower index. These are given in the second and third columns of the following Table. In the fourth column is a series of numbers in the proportion of sin 2α, the largest number being made to agree with the observed positive throw. The close agreement of the other numbers shows clearly that, on breaking the circuit, the impulse is truly proportional to sin 2α. Examination shows that the negative impulses, though in reality equal to the others, are apparently much less in amount, that they are not even in proportion, and not only this, but that the corresponding values on either side of 45° are

TABLE I.

Position of rest.	Negative throw.	Positive throw.	Calculated positive throw.
5	1	4·5	4·6
10	2	9	9·1
15	3	13	13·2
20	4·5	17	17·1
25	5	20	20·3
30	6	22·5	23
35	7	24·5	25
40	7·8	26·2	26·2
45	8·8	26·5	26·5
50	8·5	26·2	26·2
55	8·2	24·5	25
60	7·8	22	23
65	7·5	20	20·3
70	6·5	16	17·1
75	5·5	12·5	13·2
80	3·5	9	9·1
85	2	4	4·6

not the same. This want of symmetry is clearly shown by fig. 1. The discrepancy is due to the fact that the disk is brought to rest by the damping action of the field as well as by the torsion of the wire, and that the damping action is greater as the angle is less, being : : $\cos^2 \alpha$.

Fig. 1.



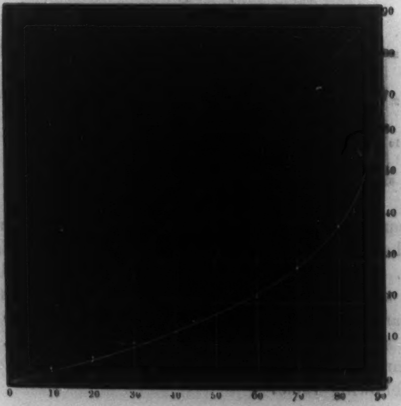
I thought it would be interesting to determine to what angle the disk would be thrown if the torsion of the wire did not act. I therefore suspended, instead of the disk, the coil used in the absolute experiments by a silk thread, adjusted the lower card by the method of no throw, and brought the index to rest successively over 10°, 20°, 30°, &c. up to 90°. The index came to rest at the series of positions shown in column 2 of the following Table:—

TABLE II.

Pointer fell	
From	To
10	3·6
20	6
30	10
40	13
45	16
50	18
60	22
70	29
80	39

The same results are shown graphically in fig. 2. It is interesting to note that the curve shown is a natural curve depending on circular functions only. It is independent of the nature of material, such as conductivity, moment of inertia, or of the strength to which the field is made to grow from

Fig. 2.



zero. It is subject to a small error, for I did not destroy the residual magnetism. That the effect of this is appreciable is evident, for in one series of experiments with a disk the throw on making was always from 45° to 33°; but the first time that the direction of the magnetizing current was changed the throw was from 45° to 35°, after which it was from 45° to 33°, as before. This diminution at the first reversal was always the same. I found almost the same fall with the half-crown as with the coil, and with one cell as with ten cells. There were slight differences, but not more than draughts from which I did not shield the needle would have accounted for. The lower angle can be read with precision, but the higher angles become difficult to observe as the damping influence diminishes. The position $\alpha = 90°$ is one of instability; for however slight a velocity is given to the disk, it will not be brought to rest for a considerable time, owing to the very minute nature of the squares of the cosines of angles nearly equal to 90°.

The last series of experiments was made with a view to determine whether the strength of field determined by observation of the throw of the disk at breaking agreed with the strength determined by some recognized method. I therefore made a small coil of twelve turns of copper wire of 1·45 centim. radius and with a resistance of 0·085 ohm. The area of the coil was 79·4 square centim. The moment of inertia of coil and index was found by comparison with a cylinder to be 58·1 units, and the torsional value of the supporting wire to be 17,000 units. The plane of the coil was adjusted by the usual method to zero, and then set to 45°. The currents from 10, 9, 8, &c. to 1 Grove cells were sent in succession through the coils of the electromagnet and through a Siemens electrodynamometer. The following Table shows the amounts of the positive and negative impulses, the strengths of the magnetizing currents in amperes, and the field-intensities calculated from the positive throws by the formula

$$H^2 = 9311000 \times \text{Throw measured in degrees.}$$

TABLE III.

Number of cells.	Magnetizing current, in amperes.	Negative throw.	Positive throw.	Calculated field, in absolute units.
10	11·85	10·5	27·5	16,000
9	11·2	9	26	15,600
8	10·44	8·2	24·5	15,100
7	9·47	7	22·5	14,500
6	8·63	6	21·3	14,100
5	7·60	4·8	19·2	13,400
4	6·53	3·3	16·5	12,400
3	5·18	2·2	13	11,000
2	3·67	1	8	8,630
1	1·83	0·2	2·8	5,070

The ends of the coil which were soldered together were then unsoldered without disturbing the soldered connexion between the torsion-wire and one end. The other end was bent so as to dip into a small mercury-cup in the axial line, so that a known current, measured by a second electrodynamometer, could be sent through the coil. During this change no part of the apparatus was moved at all; it was, however, necessary to redetermine the zero position, which was now rather more difficult, for the resistance of the torsion-wire was so great in comparison with that of the coil alone, that the throw at any angle was only about one tenth of what it was before. As before, the current from 10 to 1 cells was sent successively through the coils of the electromagnet and an electrodynamometer. The current from a Daniell cell was sent through the suspended coil and measured. In the fourth column of the following Table will be found the deflection of the coil due to currents tabulated in columns 2 and 3. In the fifth column is the deflection due to the residual magnetism; and in the sixth column the strength of field in absolute units, calculated from the formula

$$H = \frac{3{\cdot}73 \times \text{deflection in degrees}}{\text{deflecting current in absolute units} \times \cos\delta}.$$

Table IV.

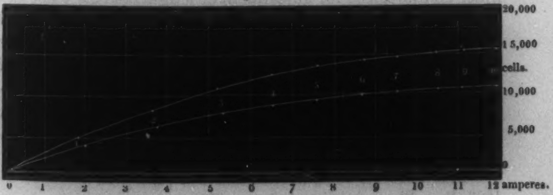
Number of cells.	Magnetizing current, in amperes.	Deflecting current, in amperes.	Deflection $=\delta$.	Deflection due to residual magnetism.	Calculated field, in absolute units.
10	11·92	·514	65	4	11,200
9	11·05	·530*	64	4	10,260
8	10·52	·502	63	4	10,320
7	9·48	·496	62·5	4	10,150
6	8·63	·480	61·5	4	10,050
5	7·60	·480	60·3	4	9,470
4	6·45	·480	59	4	8,930
3	5·14	·480	57	4	8,120
2	3·67	·480	51·5	4	6,470
1	1·98	·480	40·5	4·5	4,140

* Obviously over-estimated, hence small results.

The residual magnetism was always the same till one cell only had been employed to excite the electromagnet, when the deflection was clearly greater. This I repeated several times with one and with more than one cell: a deflection of 4½° was always obtained from one cell, and of 4° from more than one cell. To obtain a still higher residual magnetic effect, I drew the terminal along a fine wire and gradually diminished the field; by this means I obtained a residual field giving a deflection of 5°·4. The magnetic fields corresponding to the deflections 4, 4½, and 5·4 are 312, 352, and 422 absolute units.

Fig. 3 shows the field-intensity measured by the two

Fig. 3.



methods. They do not agree, nor are they quite proportional, nevertheless they are of the same order of magnitude. The discrepancy is greater than would be expected from errors of an experimental kind, even though the apparatus was hastily improvised. Nevertheless the agreement, such as it is, shows that it will be worth while to carry out a series of experiments with the accuracy and care that are needed in physical investigations. This I intend to do as soon as I am able. It will then perhaps be possible to tell whether this method of determining conductivity or field-intensity is to be relied upon: it certainly in convenience and simplicity compares very favourably with any of the usual methods.

XX. *Experiments on the Velocity of Sound in Air.*

By D. J. Blaikley[*].

[Plate XII.]

I have to bring before you this afternoon the results of a few experiments carried out in continuation of the series brought to your notice last November. Before considering the velocities obtained, however, it may be well to show by experiment the reason for the doubt in my mind as to the absolute reliability to be placed upon records obtained from membranes as used by Regnault and Le Roux; and also to explain a little more fully my reason for discarding the use of organ-pipes, speaking under a considerable pressure and with good musical tone, as used by Dulong.

If we take a short tube, say 5 inches long, with a short inner sliding-piece for adjustment of length, and close one end with a diaphragm of gold-beater's skin, against which a bead hung by silk falls, we have a very sensitive resonator for the pitch of about 512 v. If this tube were closed by a rigid material instead of by the skin, its length to give the maximum resonance to the 512 v. fork would be about 6¼ inches; but on drawing the slide to make the tube of this length there

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[*] Read June 14, 1884, in continuation of paper read November 10, 1883 (Proc. Physical Society, vol. v. p. 319).

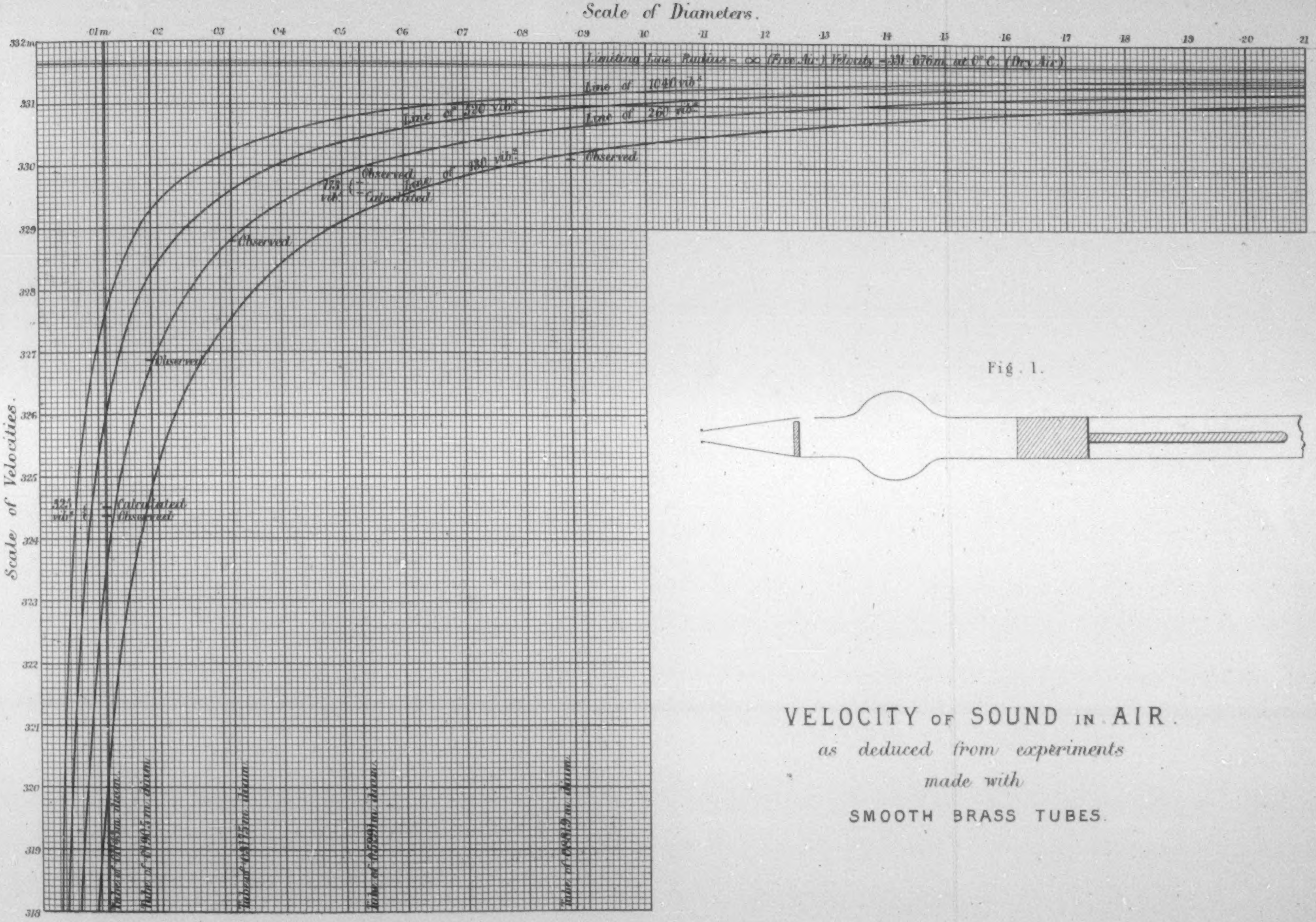


Fig. 1.

VELOCITY OF SOUND IN AIR.

as deduced from experiments
made with
SMOOTH BRASS TUBES.

Mintern Bros. lith.

is no agitation of the bead: the maximum agitation of the bead, at the present tension of the membrane, is found to be when the tube is about 5 inches long. This is its most sensitive position; but when the fork is vibrating strongly the membrane will record its action, although the length of the tube, from mouth to membrane, is somewhat greater, or less, than is necessary for best effect. Applying this to the case of a membrane stretched across a tube along which a single wave is travelling, as in Regnault's experiments, it would appear that the last possible record of the enfeebled wave would be obtained from its point of maximum condensation; but a record of the wave in the early part of its course, when it is strong, would be obtained from a point in the wave far short of its maximum condensation; so that the length measured by means of the membranes, as travelled by the wave, does not necessarily give the length passed over by a given point in the wave in the measured time. The error, small as it would be when distributed over a great length, would become more appreciable as the tube-length became shorter, and it would in every case lead to an underestimation of the velocity.

In Dulong's experiments care was taken to obtain pipes of good tone; but my experiments have convinced me that such a tone is the worst possible for measurement of wave-lengths. A good musical tone is not pure in the acoustical sense, and the presence of the partials constrains the pitch of the prime to some extent. If the form of pipe were such that its proper tones agreed exactly with the harmonic series, there would not be this difficulty of constrained pitch; but as it would have been exceedingly difficult to construct pipes of this character, I determined to introduce a bulb or pear-shaped portion between the speaking-mouth and the cylindrical tube in which the sliding-plug worked (see Plate XII. fig. 1). By this means tubes were obtained having proper tones quite out of the harmonic order, and therefore capable of giving very pure prime tones.

In November last it was stated that the results obtained from the 11·43 millim. tube were not very reliable. The experiments with this tube have been repeated, and a new tube of 88·19 millim. diameter has been introduced, completing a series of five tubes, ranging in the proportion of 3 to 5, from 11·43 to 88·19 millim. diameter*. The results of the new experiments are given in the following table :—

TABLE IV.

Velocity of Sound in dry Air, at 0° C., in tubes.

Diameter of tube......	11·43 millim.	88·19 millim.
	324·533	330·29
	324·234	330·46
		330·02
		329·72
		329·99
		330·41
		330·09
		330·06
		330·10
		330·20
Means	324·383	330·134

In Table V. the results of all the experiments are brought together :—

TABLE V.

Radius, in metres......	r ·005715	r_1 ·009524	r_2 ·015874	r_3 ·026457	r_4 ·044095
Velocity at 0° C., in metres	v 324·383	v_1 326·902	v_2 328·784	v_3 329·723	v_4 330·134
Mean pitch during observations	n 322·96	n_1 260·36	n_2 260·18	n_3 172·48	n_4 131·15
$\sqrt{\frac{1}{n}}\cdot\sqrt{\frac{1}{n_1}}$ &c. ...	·05563	·06197	·06200	·07615	·08732

From these data we may obtain a value for V = velocity in free air, where $r=\infty$, using a modification of the formula

$$v=\mathrm{V}\left(1-\frac{a}{r}\right). \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

---

* Through a clerical error the diameters of the tubes were previously given as 11·7, 19·5, 32·5, and 54·1 millim., instead of 11·43, 19·05, 31·71, and 52·91.

The formula $v = \mathrm{V}\left(1 - \frac{\alpha}{r}\right)$ gives only a fictitious value for v when r is very small; whereas v should $=0$ when $r=0$, and should $= \mathrm{V}$ when $r=\infty$.

Put F for the ratio $\frac{v}{\mathrm{V}}$, and f for $(1-\mathrm{F}) = \frac{\mathrm{V}-v}{\mathrm{V}}$. Then, when $v=0$,

$$\mathrm{F}=0 \text{ and } f=\frac{\mathrm{V}}{\mathrm{V}}=1;$$

and when $v=\mathrm{V}$,

$$\mathrm{F}=1 \text{ and } f=0.$$

When $\mathrm{F}=0$,

$$\log\frac{1}{\mathrm{F}}=\infty;$$

when $\mathrm{F}=1$,

$$\log\frac{1}{\mathrm{F}}=0.$$

Therefore in (1), where

$$\frac{\alpha}{r}=\left(1-\frac{v}{\mathrm{V}}\right)=(1-\mathrm{F}),$$

make

$$\frac{\alpha}{r}=\log\frac{1}{\mathrm{F}}=\log\frac{\mathrm{V}}{v}=\log\mathrm{V}-\log v,$$

or

$$r\left(\log\frac{\mathrm{V}}{v}\right)=r_1\left(\log\frac{\mathrm{V}}{v_1}\right). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In (1)

$$\alpha=\sqrt{\frac{\mu}{2np}}$$

(Lord Rayleigh, 'Theory of Sound,' § 347),

$$=\sqrt{\frac{\mu}{2p}}\cdot\sqrt{\frac{1}{n}},$$

so that

$$\left(\alpha-\sqrt{\frac{\mu}{2p}}\right)\propto\sqrt{\frac{1}{n}}.$$

As a slight deviation from accuracy in the relative values of $\sqrt{\frac{1}{n}}$ would affect the calculated values of V only to an exceedingly small extent, we may put

$$\sqrt{\frac{1}{n}}=\cdot 9,\quad \sqrt{\frac{1}{n_1}}=1,\quad \sqrt{\frac{1}{n_2}}=1,\quad \sqrt{\frac{1}{n_3}}=1\cdot 2,$$

$$\text{and } \sqrt{\frac{1}{n_4}}=1\cdot 4$$

in place of the values given in Table V.; and introducing these values into formulæ (1) and (2), we get

$$\frac{1\cdot4}{r_4} = \log\frac{\mathrm{V}}{v_4}\,;\ \ \frac{1\cdot2}{\frac{3}{5}r_4} = \log\frac{\mathrm{V}}{v_3},\ \text{\&c., \&c.,}$$

or

$$\log \mathrm{V} = \frac{10\log v_4 - 7\log v_3}{3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From which $\mathrm{V} = 331\cdot089.$

In the same way values for V can be found from any two values of v—as v and v_1, v and v_4, &c., as follows:—

TABLE VI.

$$\text{V as obtained from}\left\{\begin{array}{lcl}
v_4 & \text{and} & v_3 = 331\cdot089 \\
v_3 & ,, & v_2 = 332\cdot150 \\
v_2 & ,, & v_1 = 331\cdot620 \\
v_1 & ,, & v \ = 331\cdot999 \\
v_4 & ,, & v_2 = 331\cdot508 \\
v_3 & ,, & v_1 = 331\cdot881 \\
v_2 & ,, & v \ = 331\cdot746 \\
v_4 & ,, & v_1 = 331\cdot540 \\
v_3 & ,, & v \ = 331\cdot620 \\
v_4 & ,, & v \ = 331\cdot603
\end{array}\right.$$

$$\text{Mean} \ . \ . \ . = 331\cdot676$$

As v_1 and v_2 have practically the same values for n, V as obtained from this pair of velocities is uninfluenced by the factor $\sqrt{\frac{1}{n}}$; and if the influence of n is properly represented by $\sqrt{\frac{1}{n}}$, the mean of all the values of V should agree with V as obtained from v_1 and v_2. The mean is 331·676 metres; and the latter value is 331·620, with which the mean is in very close agreement. The pairs of adjacent values v_4 and v_3 &c. are rather ill-conditioned for the determination of V: the best value of V should be from the extreme values of v—that is, the pair v_4 and v. This value is 331·603—very little different from the value 331·620 obtained from v_2 and v_1, where there is no variation in the value of $\sqrt{\frac{1}{n}}$. From these results it would appear that the influence of the vibrational rate of stationary waves in tubes upon the velocity is properly represented by

$\sqrt{\frac{1}{n}}$; but as Lord Rayleigh, in the paragraph quoted, refers to Schneebeli's and A. Seebeck's investigations, based upon Kundt's experiments, we may calculate a value for V upon their determinations. According to these observers, when n varies, the diminution of velocity is proportional rather to $\sqrt{\frac{1}{n^3}}$ than to $\sqrt{\frac{1}{n}}$. Taking the pair of velocities v and v_4, and substituting $\sqrt{\frac{1}{n^3}}$ for $\sqrt{\frac{1}{n}}$, we get $V = 334{\cdot}439$—manifestly too high, and very different from 331·620, the value obtained from the pair v_1 and v_2.

In the diagram (Plate XII.) and in Table VIII. I have therefore used $\sqrt{\frac{1}{n}}$; but this, or any modification of it such as $\sqrt[n]{\frac{1}{n^m}}$, can only be applicable, and then but approximately, within certain limits.

TABLE VII. TABLE VIII.

Calculated velocity, in metres, at the pitch of 260 vibrations.	Comparison between values of v, v_1, v_2, v_3, v_4, as observed and as calculated, at the pitch of observations, V being taken as 331·676 metres.							
	Radius.		Velocity, in metres.			Differences.		n, or pitch.
				Observed.	Calculated.	−	+	
323·728	r	·005715	v	324·383	324·514	...	·131	322·96
326·884	r_1	·009524	v_1	326·902	326·884	·018	....	260·36
328·792	r_2	·015874	v_2	328·784	328·792	...	·008	260·18
329·943	r_3	·026457	v_3	329·723	329·545	·178	...	172·48
330·635	r_4	·044095	v_4	330·134	330·209	...	·075	131·15

In the diagram (Plate XII.) the curve given by the figures in Table VII. is laid down, and also the observed and calculated values given in Table VIII. To these are added curves for 130, 520, and 1040 vibrations.

In addition to the experiments of which the details are given, many trials were made in the course of adjusting the apparatus. Some of these trials were at pitches other than those finally adopted; and although such results were of no value for exact comparison, the general bearing of them was quite in agreement with the results tabulated. One of these preliminary trials was a set of five observations with the tube of 52·91 millim. diameter (r_3) at the pitch of 260. The mean result was a velocity of 330·27, in place of 329·94 as on Table VII. This trial was made with the tube before the introduction of the bulb-mouth; and the third partial tone was perceptible to the ear, so that the prime may have been influenced a little thereby.

The notes were all purposely kept very weak, so that the excess of pressure in the tubes when sounding, above the barometric pressure, must have been very small indeed. In one of the large tubes (r_3) a water-pressure gauge was introduced; but the pressure was barely measurable, certainly not exceeding $\frac{1}{50}$ inch of water. In the calculations I have therefore assumed that the influence of intensity might be neglected.

The chief conclusions to which these experiments appear to lead are the following:—

1st. The tubes used for the measurement of wave-length, as determined by the length between nodes, must speak with a pure tone; or

2nd. If partials are present, the tubes must be of such form as to have their proper tones in exact agreement with the harmonic series. (Neither of these conditions is easily attainable with ordinary organ-pipes.)

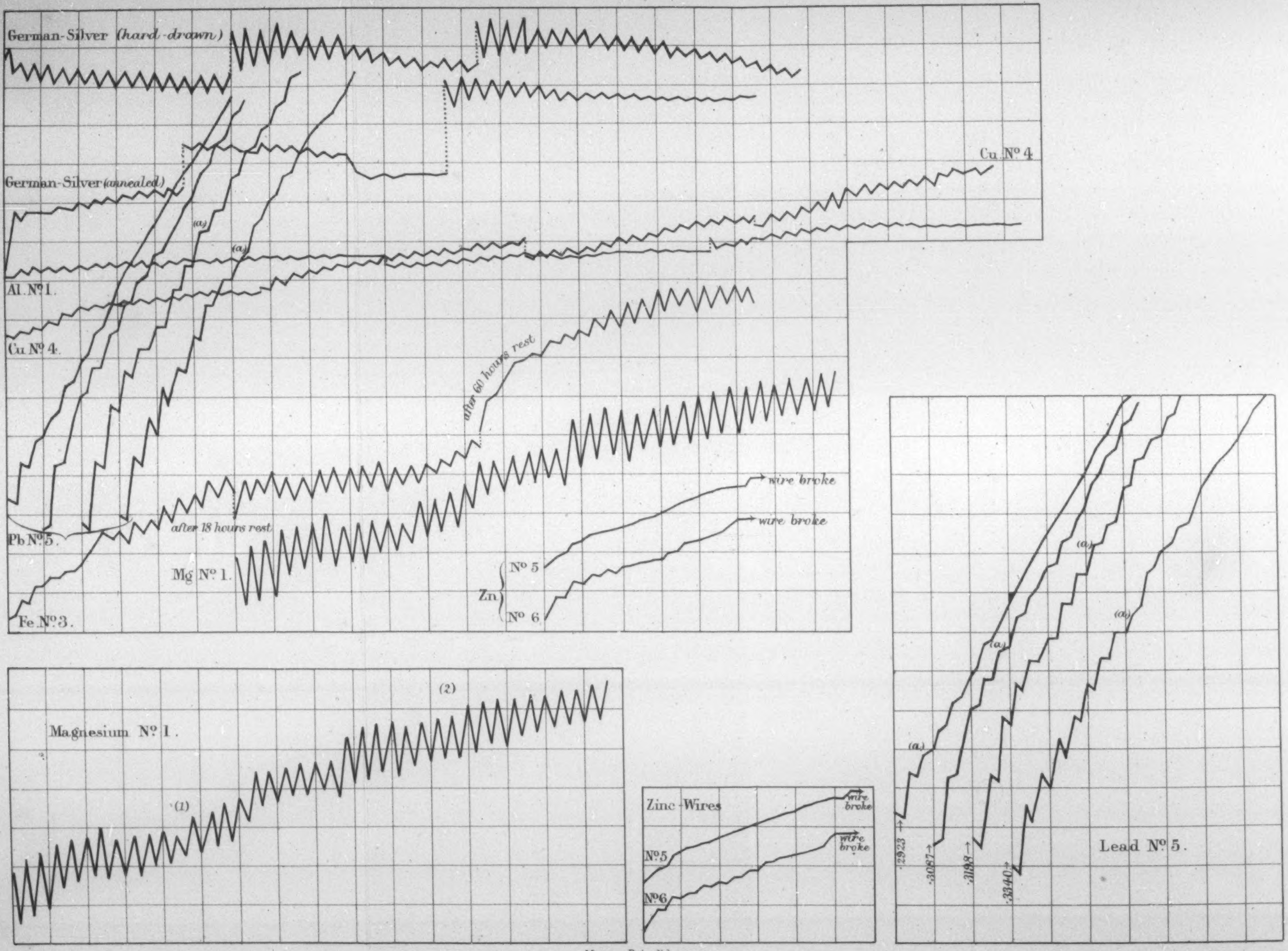
3rd. The air-blast must not constrain the pipe to speak any other pitch than its natural pitch of resonance.

4th. In smooth tubes the diminution of velocity is proportional to r^{-1} and to $n^{-\frac{1}{2}}$, as determined by Helmholtz.

5th. The velocity V in free air for sound-waves of low intensity, or just audible, is 331·676 metres at 0° C.

6th. The ratio between the two specific heats of air, as deduced from the Newtonian velocity 279·955 metres, and V as above 331·676 metres, is 1·4036.

As there is perhaps room for some doubt about the influence of n being properly represented by $n^{-\frac{1}{2}}$, I have not attempted to employ Kirchhoff's equation in place of Helmholtz's; but in abler hands than mine, the experimental results may perhaps be of some assistance in determining one or more of the points involved in these formulæ.



Mintern Bros. lith.

XXI. *On the Alterations in the Electrical Resistances of Metallic Wires, produced by Coiling and Uncoiling.* By JAMES HOPPS, *Superintendent of Workshops, Royal Indian Engineering College, Cooper's Hill*[*].

[Plate XIII.]

DURING the past winter, while assisting a pupil to make some resistance-coils, I was struck with the great difference that often existed between the resistance of the wire before it was coiled on to its bobbin and after; the difference was not always constant or proportional to the length of the wires used, and appeared to be largely influenced by the tension with which the wires were coiled on to the bobbins.

Some of the coils altered so much after winding as to lead to the supposition of their being short-circuited; and on uncoiling several of these and recoiling at a lower tension, the resistance would alter considerably.

The diameter of the bobbin used also appeared to have great influence in producing changes in the resistance.

A great portion of the alterations appeared to be temporary.

As has been observed above, the differences were not always constant; neither were they regular in their signs, *i. e.* they would sometimes show an increase and sometimes a decrease of resistance, but generally the change would be one of increase.

Having resolved to make some efforts to clear up this matter, I first sought to find what had been done by others in this direction. A very careful search through books and also of the Transactions of the Royal Society afforded no evidence that this field had been even entered upon, *i. e.* any attempt by experiment or otherwise to determine and account for the effects of coiling and uncoiling on the electrical resistance of metallic wires.

After experimenting some weeks, I purposely attended the meeting of this Society on February 23rd to hear a paper, "On the Adjustment of Resistance-Coils," by Prof. Silvanus P. Thompson; and although some of the difficulties in the way of adjusting resistance-coils were spoken of, yet the difficulty that had given us so much trouble was not once alluded to, either in the paper or in the discussion which followed. At the close of the proceedings, in the course of a short conversation with Prof. Thompson, and in reply to a question from myself, he stated that he had observed that the resistance of a wire was altered by being coiled. Mr. Latimer Clark also observed that he had noticed the change, but added that the changes were not always constant, giving sometimes an increase and sometimes a decrease in the resistance. Now experiments had given me the same results, and had the subject cropped up during the discussion, I had prepared a few notes to give to the meeting.

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[*] Read June 28th, 1884.

The fact of having obtained sometimes + and sometimes − readings had puzzled me much, but after the conversation above alluded to I resolved to continue my experiments; and although these are yet far from complete, I have felt it my duty to lay the results already obtained before the Society.

Before going into a description of the apparatus and method employed (part of the apparatus is before you), I would crave a few moments to allude to some of my earlier experiments. These were conducted in a very primitive way; but the results obtained, although appearing so erratic and contradictory, have been in a great measure confirmed by using the more elaborate method employed later on. In confirmation of this I would draw your attention to the great resemblance which exists between the two curves on the diagram, which are the curves of copper wires produced by hand- and machine-winding respectively.

The method first employed to investigate this effect was to let the wire under test form one side of a Wheatstone bridge, doubling the wire into a loop as in a resistance-coil, and rolling it by hand on to a cylinder or other shapes in wood. The resistance could thus be taken after each operation without the necessity of altering the connexions.

The time lost in waiting until the heat imparted to the wire through handling had disappeared was great, and the uncertainty as to the tension with which the wire was coiled and uncoiled caused me to seek some other method.

After many schemes the one before you was adopted. Bearing in mind that many of the wires to be experimented upon would not be insulated, and would be of many different diameters and rigidities, it was very early evident that the drum on which the wires were to be coiled would also have to insulate each convolution from its neighbour as well as to wind up the wire. The different diameters and rigidities also determined the necessity of being able to vary the tension. The insulation is obtained by using an ebonite drum to receive the wire; on this drum a right- and left-handed screw has been cut. The variation in the tension may be obtained in two different ways, or by a combination of both:—1st, by altering the load carried in the little waggon which runs up and down the inclined plane; 2nd, by altering the angle of inclination of the plane; or we may combine both if necessary.

As the application of longitudinal strain to a wire while being tested for resistance has been shown to be considerable, it was necessary to relieve the wire from the strain due to the load before taking the resistance, otherwise the changes due to strain would have been included in the readings. To remove the strain, the waggon on arriving at the bottom of the plane rests against a stop; on being drawn to the top the plane is brought to a position slightly above the horizontal; these allowing in both cases the drum to slightly unwind itself, and consequently the strain on the wire is almost entirely removed.

The ebonite drum, as before observed, has a right- and left-handed screw cut upon it; these meet in the middle of its length. A screw holding down an ebonite cap here passes through the inside of the loop of the wire under test, and fixes it firmly, but without injury, to the drum; the ends of the wire are carried up the plane to two binding-screws, and with the necessary leading wires form one side of a Wheatstone bridge.

A long length of stout whipcord is attached to the middle of a winding drum underneath the head of the plane, and the ends, after being coiled between the empty threads of the ebonite drum (starting from the centre), are fixed to the ends of the drum. On turning the drum below, the cords pull on the top part of the ebonite drum, causing it to revolve; and at the same time that the cord is being payed off, the wire under test is being coiled on in its place. This is continued until the waggon arrives at the top; a pawl working on a ratchetwheel prevents the waggon running back until the plane has been brought to a horizontal position, where, after resting five minutes, the resistance is taken. The operations are now reversed; and after a similar rest at the bottom, the resistance is again taken. And these operations are repeated, each operation taking about six minutes, giving an average of ten per hour; they were generally continued for three hours, giving for each series about thirty readings, and then allowed to stand until the following evening, all strain being previously removed.

The temperature of the laboratory was carefully regulated each evening, for two hours before commencing work, to the same temperature as on the previous evening, and kept constant within half a degree Fahr. ±.

In the case of some wires as many as 380 readings have been taken altogether; this was on lead wire No. 5. At the end of the seventh series the wire broke.

The curves of resistance of four of the seven series of tests on this wire is very interesting. It will be observed that, while being very similar to each other, there is a point marked (*a*) on each series where coiling and uncoiling produce an increase in the resistance. Again, the wonderful power of recovery which is shown by the wire after each rest is very marked; the normal condition would appear to be to give positive and negative readings, and that this condition is upset after a time. The inability to recover this condition has suggested that, when this point has been arrived at, it might be said to represent the commencement of a kind of electrical fatigue.

There are some other points on this diagram, and which are more or less repeated by every other wire that I have tested, which furnish matter for speculation; such as—why should coiling generally produce a less effect than uncoiling? and why should the signs be generally different? and why should those signs in many cases become reversed?

An *increase* of resistance on uncoiling and a *decrease* on coiling take place with lead, copper, German silver, aluminium, and magnesium; and also with the first few operations on soft iron wire, after which the signs are completely changed.

An increase almost invariably follows coiling and uncoiling with zinc, but the effect of coiling varies from one half to one thirtieth of the effect of uncoiling.

The difference between coiling and uncoiling, or, we might say, the amplitude of the differences of resistances, is greatest in the case of magnesium and least in the case of aluminium; the latter, on referring to the curves, will be seen to alter very little indeed.

The amplitude of the differences in the case of hard-drawn German silver is not so great after a few series; and when annealed, after showing great increases after standing at rest, the final series approach very near to that of the hard-drawn wire, which is strong evidence indeed that the wire has become harder through repeated coiling and uncoiling.

The length of the wires were very carefully taken before and after the experiments, and the necessary calculations made for alterations in length and cross-section according to the formula $R \propto \frac{l}{a}$, in which $R =$ the resistance, $l =$ the length, and $a =$ the area of the cross section.

After making these corrections, the changes in the resistance remaining unaccounted for are:—

Metals.	Of the increase on the original resistance.	Of the actual observed change.
Iron	2·3 per cent.	81·64 per cent.
Lead (average of six)	1·27 „	2·91 „
Copper	1·18 to 1·42 per cent.	57·58 to 60·7 per cent.
Zinc	1·23 to 2·16 „	23·6 to 42·4 „
Aluminium	0·77 to 2·206 „	41·15 to 72·01 „
German silver (annealed) ...	0·054 to 0·171 „	11·89 to 21·6 „
Magnesium No. 2...............	1·549 per cent.	

With magnesium No. 2, from a different sample from No. 1, the wire became shorter; and the resistance, which should have fallen ·0745 per cent., actually increased 1·475 per cent., being equivalent to a difference of 1·549 per cent. on the original resistance unaccounted for.

With magnesium No. 1 the actual increase of resistance amounted to 2·16 per cent. on the original resistance, whereas theoretically it should have increased 3·39 per cent., or 1·23 per cent. greater than really took place; or we may say that of the theoretical increase only 54·35 per cent. was visible, showing that the specific conductivity of the wire had risen. Four portions of this wire were tested, and the results were all very near alike.

On examining the results obtained with German silver No. 5 (annealed), which after all is most likely to interest us, owing to its employment in resistance-coils, we find that the total increase was equal to ·454 per cent.; and after deducting ·4 per cent., which is due to increase in length and diminution of section, there still remains unaccounted for ·054 per cent. on the original resistance, or 11·89 per cent. of the whole observed change.

With German silver (hard-drawn) the results are very curious. Here the length actually decreased; and on making the necessary corrections, the resistance should have shown a decrease of ·284 per cent.; but the actual decrease was only equal to ·036 per cent., not low enough by ·248 per cent.; or we may say that of the theoretical decrease only 12·26 per cent. was visible.

On examining the curves from the iron wires Nos. 3 and 4, it will be observed that at the commencement uncoiling produced a very large *increase*, while coiling produced a small *decrease*; but after sixteen operations in one case and twenty-one in the other, the signs became reversed, and this continued throughout the remaining series of the two wires.

On page 74, vol. vi. of the 'Proceedings of the Physical Society,' I find a paper by Mr. Herbert Tomlinson, in which he says that "the behaviour of nickel is especially worthy of notice, because in it longitudinal traction, when not carried beyond a certain limit, *diminishes* the electrical resistance in spite of the increase of length and diminution of section which ensues."

I have not been able to obtain wires in nickel, but, according to the results obtained, some samples of magnesium appear to have the same property.

At the last moment Prof. Stocker has shown me that in *Die Electricität*, by Wiedemann, it is noted that "the coiling of a copper or iron wire increases, whilst the uncoiling diminishes the specific resistance about 0·003 of the total value of the same."

And, again, in *Die Physik*, vol. iii., by Mousson, that "the coiling of a wire upon a cylinder slightly increases the resistance, in consequence, as is supposed, of tension; uncoiling diminishes it again. Under similar circumstances, the changes amounted to 0·0032 in the case of copper and to 0·0056 in iron, of their total resistances."

It will be observed that both these descriptions are contrary to what I must conclude from my own experiments.

Having made some inquiries from a friend of mine who had charge of the testing department in the cable factory of J. B. Pirelli, F. Casassa et C^{ie}, of Milan, he has supplied me with data which show that the specific conductivity of the copper conductors have fallen in many cases 1½ per cent. during manufacture, and when encased in lead tubes they have often fallen over 2 per cent. In all cases the necessary corrections have been made for increase of length and diminution of section due to strain in passing through the covering machines. Possibly the greater loss in the lead-encased core may be due to a damping-effect from the lead, but the bulk of the increase of resistance must be due to some other cause. These cables were manufactured under very strictly enforced conditions for the Italian State Telegraph-stores; and the tests taken by government officials, ten weeks after they had been sent from the factory, were in all cases within 0·2 per cent. of the final tests in the factory, showing conclusively that the changes were in a great measure permanent.

I have therefore come to a very decided conclusion that the changes in the resistance are not altogether the result of changes in form, and that their cause must be sought for elsewhere.

Many theories have suggested themselves, but none are entirely satisfactory.

One theory was that, in coiling, the decrease of resistance was due to a thickening of the wire on its internal side and a thinning of the external side, thus bringing the centre of area inwards, and so making the actual distance the current would have to travel shorter, which would be equivalent to making the wire shorter; and then on uncoiling, the displacement of the molecules, due to slipping on each other when seeking to regain their original position, would have the effect of increasing their distance apart, and consequently increasing the resistance. But the weak point in this theory is that it will not account for the change of signs which so often takes place, nor will it account for the zinc wires giving increased resistances on coiling.

Another theory, which appears more promising, was that, while being coiled and uncoiled, the wires were subject to strains of a torsional kind, which might be due to their having a certain amount of residual twist in them, owing to the way in which they have been coiled on to the drums on the bench of the wire drawer; and that on being coiled and uncoiled on their bobbins this twist might be increased or decreased, so giving different amounts in the resistance. But from experiments I have made, which seem to me quite conclusive, it appears that although there is a certain amount of twisting and untwisting produced by being wound on to the bobbins, yet this fails to account for the residue of the observed changes.

With reference to the effects on the permanency of value of a set of resistance-coils which are only subjected to one winding, I have not yet sufficient data to lay before you ; but, so far as I have gone into this part of the subject, I believe that the immediate alterations on coiling the wires on the bobbins are to a great extent affected by the tension and the speed with which they are wound, the thickness and kind of insulator employed (cotton-covered wires appear to be less affected than silk-covered wires), and also by the diameter of the bobbins on which the wire is wound (the smaller the bobbin the greater the alteration). But further experiments are necessary to put these beyond doubt.

Appended to this paper are a few tables showing the actual readings in the first series of several of the wires tested (these readings include the resistance of the leading wires, ·0274). These, together with the curves (Pl. XIII.), may be of some service in assisting to a conclusion as to the probable cause of the changes in the resistance of wires produced by coiling and uncoiling.

Actual Readings and Differences produced by Coiling and Uncoiling of Lead Wire No. 5 (first four series only).

U represents uncoiled ; C represents coiled.

	1st Series.		2nd Series.		3rd Series.		4th Series.	
	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.
U	·2923	+·0001	·3087	+·0001	·3198	−·0002	·3340	−·0001
C	22	+·0011	88	+·0015	·3196	+·0017	39	+·0017
U	33	−·0001	·3103	+·0001	·3213	−·0002	56	−·0004
C	32	+·0007	04	+·0008	11	+·0017	52	+·0012
U	39	+·0001	12	+·0008	28	−·0002	64	−·0004
C	40	+·0005	20	+·0001	26	+·0011	60	+·0012
U	45	+·0002	28	......	37	−·0002	72	−·0004
C	47	+·0005	28	+·0008	35	+·0007	68	+·0010
U	52	+·0002	36	+·0001	42	......	78	−·0001
C	54	+·0005	37	+·0006	42	+·0007	77	+·0009
U	59	+·0002	43	+·0001	49	......	86	−·0001
C	61	+·0006	44	+·0005	49	+·0008	85	+·0008
U	67	+·0002	49	+·0002	57	......	93	......
C	69	+·0004	51	+·0006	57	+·0007	93	+·0007
U	73	+·0004	57	+·0001	64	......	·3400	......
C	77	+·0004	58	+·0005	64	+·0008	00	+·0005
U	81	+·0003	63	+·0001	72	+·0001	5	+·0002
C	84	+·0004	64	+·0005	73	+·0005	7	+·0007
U	88	+·0003	69	+·0002	78	+·0001	14	+·0002
C	91	+·0003	71	+·0006	79	+·0007	16	+·0004
U	94	+·0004	77	+·0003	86	+·0001	20	+·0002
C	98	+·0003	80	+·0005	87	+·0006	22	+·0004
U	·3001	+·0003	85	+·0002	93	+·0001	26	+·0002
C	4	+·0003	87	+·0005	94	+·0005	28	+·0004
U	7	+·0003	92	+·0002	99	+·0001	32	+·0004
C	10	+·0004	94	+·0004	·3300	+·0005	36	+·0003
U	14	+·0003	98		5	+·0001	39	+·0002
C	17	+·0003	Rested here 21 hours ; no change on resuming.		6	+·0006	41	+·0002
U	20	+·0004			12	+·0002	43	+·0003
C	24	+·0004			14	+·0005	46	+·0003
U	28	+·0002			19	+·0001	49	+·0004
C	30	+·0004			20	+·0005	53	+·0003
U	34	+·0004			25	+·0002	56	+·0003
C	38	+·0002			27	+·0006	59	+·0003
U	40	+·0002			33	+·0003	62	+·0003
C	42	+·0003			36	+·0004	65	+·0003
U	45	+·0002			40		68	+·0003
C	47	+·0004			Rested here 22 hours ; no change on resuming.		71	+·0004
U	51	+·0005					75	+·0004
C	56	+·0003					79	+·0003
U	59	+·0003					82	+·0003
C	62	+·0004					85	+·0002
U	66	+·0003					87	+·0003
C	69	+·0003					90	+·0003
U	66	+·0004					93	+·0003
C	70	+·0006					96	+·0003
U	76	+·0003					99	+·0003
C	79	+·0004					·3502	+·0003
U	83	+·0004					5	+·0003
C	87	+·0003					8	+·0001
U	90	......					9	
C	90						Loss after standing 21 hours=·0003.	

Aluminium Wire.

	No. 1.			
	1st Series.		2nd Series.	
	Resistance.	Difference.	Resistance.	Difference.
U ...	·08004		·08042	
C ...	4	......	37	−·00005
U ...	22	+·00018	48	+·00011
C ...	15	−·00007	42	−·00006
U ...	26	+·00011	49	+·00007
C ...	18	−·00008	43	−·00006
U ...	28	+·00010	53	+·00010
C ...	22	−·00006	47	−·00006
U ...	32	+·00010	58	+·00011
C ...	25	−·00007	53	−·00005
U ...	34	+·00009	61	+·00008
C ...	27	−·00007	56	−·00005
U ...	37	+·00010	64	+·00008
C ...	26	−·00011	59	−·00005
U ...	35	+·00009	67	+·00008
C ...	30	−·00005	63	−·00004
U ...	38	+·00008	69	+·00006
C ...	33	−·00005	66	−·00003
U ...	41	+·00008	71	+·00005
C ...	35	−·00006	68	−·00003
U ...	44	+·00009	72	+·00004
C ...	39	−·00005	68	−·00004
U ...	46	+·00007	73	+·00005
C ...	42	−·00004	69	−·00004
U ...	48	+·00006	74	+·00005
C ...	44	−·00004	71	−·00003
U ...	49	+·00005	76	+·00005
C ...	46	−·00003	73	−·00003
U ...	52	+·00006	77	+·00004
C ...	48	−·00004	74	−·00003
U ...	55	+·00007	78	+·00004
C ...	52	−·00003	75	−·00003
U ...	60	+·00008	79	+·00004
C ...	56	−·00004	76	−·00003
U ...	61	+·00005	81	+·00005
C ...	58	−·00003	78	−·00003
U ...	61	+·00003	83	+·00005
C ...	59	−·00002	79	−·00004
U ...	62	+·00003	82	+·00003
C ...	60	−·00002	79	−·00003
U ...	63	+·00003	82	+·00003
C ...	61	−·00002	80	·00002
U ...	63	+·00002	82	+·00002
C ...	62	−·00001		
U ...	64	+·00002		
C ...	63	−·00001		
U ...	64	+·00001		
C ...	64	......		
U ...	65	+·00001		
C ...	65	......		
U ...	66	+·00001		

Rested here 21 hours; loss by standing ·00023.

Rested here 45 hours; and gained by standing ·00019.

German-silver Wires.

	No. 4 (hard drawn).				No. 5 (annealed).			
	1st Series.		2nd Series.		1st Series.		2nd Series.	
	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.
U...	1·53483		1·53541		1·51821		1·52150	
C...	25	−·00058	445	−·00096	982	+·00161	140	−·00010
U...	62	+·00037	552	+·00107	963	−·00019	150	+·00010
C...	12	−·00050	458	−·00094	981	+·00018	142	−·00008
U...	65	+·00053	545	+·00087	980	−·00001	149	+·00007
C...	13	−·00052	468	−.00077	980	......	138	−·00011
U...	60	+·00047	556	+·00088	980	......	150	+·00012
C...	05	−·00055	471	−·00085	992	+·00012	136	−·00014
U...	45	+·00040	530	+·00059	992	......	130	+·00006
C...	02	−·00043	485	−·00045	988	−·00004	122	−·00008
U...	42	+·00040	524	+·00039	1·52000	+·00012	140	+·00018
C...	03	−·00039	480	−·00044	1994	−·00006	123	−·00017
U...	42	+·00039	518	+·00038	2004	+·00010	135	+·00012
C...	05	−·00037	482	−·00036	2000	−·00004	120	−·00015
U...	41	+·00036	516	+·00034	2010	+·00010	132	+·00012
C...	00	−·00041	478	−·00038	2003	−·00007	119	−·00013
U...	40	+·00040	501	+·00023	2020	+·00017	129	+·00010
C...	00	−·00040	472	−·00029	2010	−·00010	111	−·00018
U...	36	+·00036	499	+·00027	2025	+·00015	120	+·00009
C...	00	−·00036	66	−·00033	2014	−·00011	108	−·00012
U...	35	+·00035	85	+·00019	2031	+·00017	114	+·00006
C...	1·53396	−·00039	59	−·00026	2021	−·00010	100	−·00014
U...	434	+·00038	80	+·00021	2038	+·00017	085	+·00015
C...	395	−·00039	52	−·00028	2027	−·00011	073	−·00012
U...	434	+·00039	73	+·00021	2040	+·00013	062	+·00011
C...	394	−·00040	37	−·00036			068	−·00006
U...	423	+·00029	62	+·00025			071	+·00003
C...	390	−·00033	48	−·00014	Rested for 16 hours; gained ·00110.		065	−·00006
U...	421	+·00031	62	+·00014			070	+·00005
C...	390	−·00031	34	−·00028			070	......
U...	425	+·00035	58	+·00024			071	+·00001
C...	391	−·00034	31	−·00027			070	−·00001
U..	425	+·00034	52	+·00021			072	+·00002
C...							070	−·00002
U...	Rested for 21 hours; gained ·00116.		Rested for 21 hours; gained ·00109.				073	+·00003
							Rested for 26 hours; gained ·00231.	

Magnesium Wires.

	No. 1. Length at commencement =55·08 inches.				No. 2. Length at commencement =86 inches.			
	1st Series.		2nd Series.		1st Series.		2nd Series.	
	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.
U...	·29195		·29488		·44079		·44312	
C...	60	−·00135	384	−·00104	3815	−·00264	148	−·00164
U...	210	+·00150	525	+·00141	4148	+·00333	368	+·00220
C...	75	−·00135	410	−·00115	3933	−·00215	205	−·00163
U...	225	+·00150	555	+·00145	4216	+·00283	404	+·00199
C...	98	−·00127	427	−·00128	3991	−·00225	232	−·00172
U...	255	+·00157	567	+·00140	4245	+·00254	381	+.00149
C...	145	−·00110	445	−·00122	4023	−·00222	223	−·00158
U...	265	+·00120	567	+·00122	257	+·00234	385	+·00162
C...	155	−·00110	435	−·00132	062	−·00195	231	−·00154
U...	280	+·00125	565	+·00130	272	+·00210	386	+·00155
C...	180	−·00100	465	−·00100	091	−·00181	235	−·00151
U...	303	+·00123	575	+·00110	300	+·00209	380	+·00145
C...	178	−·00125	473	−·00102	126	−·00174	242	−·00138
U...	277	+·00099	585	+·00112	325	+·00199	381	+·00139
C...	186	−·00091	482	−·00103	168	−·00157	241	−·00140
U...	284	+·00098	594	+·00112	230	+·00062	384	+·00143
C...	185	−·00099	488	−·00106	088	−·00142	246	−·00138
U...	292	+·00107	605	+·00117	248	+·00160	381	+·00135
C...	205	−·00087	496	−·00109	081	−·00167	242	−·00139
U...	295	+·00090	610	+·00114	251	+·00170	380	+·00138
C...	205	−·00090	505	−·00105	089	−·00162	241	−·00139
U...	285	+·00080	617	+·00112	250	+·00161	376	+·00135
C...	225	−·00060	505	−·00112	084	−·00166	244	−·00124
U...	327	+·00102	620	+·00115	245	+·00161	368	+·00129
C...	237	−·00090	525	−·00095	085	−·00160	239	−·00129
U...	345	+·00108	625	+·00100	246	+·00161	370	+·00131
C...	250	−·00095	535	−·00090	100	−·00146	241	−·00129
U...	362	+·00112	622	+·00087	249	+·00149	368	+·00127
C...	265	−·00097	545	−·00077	112	−·00137	240	−·00128
U...	377	+·00102	645	+·00100	251	+·00139	354	+·00114
C...	314	−·00063	547	−·00098			242	−·00112
U...	434	+·00120	647	+·00100			350	+·00108
C...	355	−·00079	566	−·00081			235	−·00115
U...	438	+·00083	660	+·00094			351	+·00116
C...	366	−·00072	573	−·00087			239	−·00112
U...	445	+·00079	667	+·00094			344	+·00105
C...	385	−·00060					238	−·00106
U...	458	+·00073					341	+·00103
C...	390	−·00068					237	−·00104
U...	462	+·00072					342	+·00105
C...	397	−·00065						
U...	468	+·00071						
	Rested here 21 hours; resistance rose to ·29488; showing gain by standing of ·00020.		Rested here 21 hours; gained ·00021.		Rested here 18 hours; gained by standing ·00061.		Rested here 26 hours; gained by standing ·0003.	

Iron Wires (soft).

	No. 3.				No. 4.			
	1st Series.		2nd Series.		1st Series.		2nd Series.	
	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.
U...	·34735	+·00007	·34995	+·00094	·34720	+·00015	·34970	+·00090
C...	42	+·00032	·35089	−·00067	35	+·00043	·35060	−·00045
U...	74	−·00002	022	+·00071	78	−·00006	15	+·00050
C...	72	+·00040	093	−·00046	72	+·00043	65	−·00037
U...	812	−·00004	047	+·00054	·34815	+·00001	28	+·00046
C...	16	+·00026	101	−·00059	16	+·00021	74	−·00044
U...	42	+·00005	042	+·00045	37	+·00005	30	+·00038
C...	47	+·00015	097	−·00058	42	+·00018	68	−·00033
U...	62	+·00008	039	+·00059	60	+·00008	35	+·00042
C...	70	+·00016	098	−·00050	68	+·00012	77	−·00045
U...	86	+·00016	048	+·00056	80	+·00018	32	+·00038
C...	902	+·00012	104	−·00046	98	+·00022	70	−·00039
U...	14	+·00018	058	+·00049	·34920	+·00010	31	+·00048
C...	32	−·00004	107	−·00050	30	......	79	−·00037
U...	28	+·00028	057	+·00058	30	+·00010	42	+·00046
C...	56	−·00036	115	−·00059	40	−·00010	88	−·00043
U...	20	+·00052	056	+·00061	30	+·00023	45	+·00054
C...	72	−·00020	117	−·00055	53	−·00023	99	−·00030
U...	52	+·00040	062	+·00062	30	+·00038	69	+·00050
C...	92	−·00028	124	−·00066	68	−·00028	·35119	−·00034
U...	64	+·00051	058	+·00060	40	+·00024	085	+·00043
C...	·35015	−·00033	118	−·00042	64	−·00019	128	−·00016
U...	4982	+·00059	076	+·00038	45	+·00020	112	+·00033
C...	5041	−·00039	114	−·00030	65	−·00015	45	−·00021
U...	5002	+·00056	084	+·00034	40	+·00035	24	+·00035
C...	58	−·00039	118	−·00016	75	−·00025	59	−·00015
U...	19	+·00060	102	+·00040	50	+·00048	44	+·00036
C...	79	−·00041	142	−·00021	98	−·00030	80	−·00010
U...	38	+·00058	121	+·00043	68	+·00046	70	+·00029
C...	96	−·00041	164	−·00019	·35014	−·00026	99	−·00009
U...	55		145	+·00047	·34988	+·00062	90	+·00036
C...			192	−·00016	·35050	−·00028	·35226	−·00007
U...			176		32	+·00056	19	+·00049
C...					88	−·00023	68	−·00012
U...					65		56	
	Rested here 45 hours; loss by standing = ·00060.		Rested here 45 hours; gained by standing = ·00029.		Rested here 21 hours; loss by standing ·00095.		Rested here 21 hours; loss by standing = ·00026.	

Copper Wire.

	No. 4.			
	1st Series.		2nd Series.	
	Resistance.	Difference.	Resistance.	Difference.
U	·17762	−·00003	·17882	−·00002
C	59	+·00019	·17880	+·00023
U	78	−·00003	·17903	−·00009
C	75	+·00013	·17894	+·00020
U	88	−·00003	·17914	−·00010
C	85	+·00012	04	+·00024
U	97	−·00003	28	−·00008
C	94	+·00014	20	+·00016
U	·17808	−·00004	36	−·00006
C	04	+·00021	30	+·00011
U	25	−·00005	41	−·00007
C	20	+·00011	34	+·00014
U	31	−·00004	48	−·00005
C	27	+·00012	43	+·00017
U	39	−·00005	60	−·00008
C	34	+·00009	52	+·00015
U	43	−·00005	67	−·00008
C	38	+·00009	59	+·00014
U	47	−·00004	73	−·00008
C	43	+·00011	65	+·00013
U	54	−·00005	78	−·00007
C	49	+·00011	71	+·00013
U	60	−·00005	84	−·00007
C	55	+·00009	77	+·00012
U	64	−·00005	89	−·00007
C	59	+·00007	82	+·00011
U	66	−·00003	93	−·00006
C	63	+·00008	87	+·00010
U	71	−·00004	97	−·00006
C	67	+·00007	91	+·00007
U	74	−·00004	98	−·00007
C	70	+·00007	91	+·00008
U	77	−·00003	99	−·00003
C	74	+·00006	96	+·00009
U	·17880		·18005	
	Rested here 21 hours; gained by standing ·00002.		Rested here 21 hours; loss by standing ·00039.	

Zinc Wires.

	No. 5.		No. 6.	
	Resistance.	Difference.	Resistance.	Difference.
U	·14063		·14038	
C	077	+·00014	065	+·00027
U	095	+·00018	090	+·00025
C	104	+·00009	087	−·00003
U	128	+·00024	119	+·00032
C	135	+·00007	117	−·00002
U	146	+·00011	138	+·00021
C	149	+·00003	138	......
U	160	+·00011	152	+·00014
C	164	+·00004	149	−·00003
U	173	+·00009	164	+·00015
C	178	+·00005	163	−·00001
U	186	+·00008	178	+·00015
C	190	+·00004	180	+·00002
U	200	+·00010	191	+·00011
C	205	+·00005	193	+·00002
U	212	+·00007	205	+·00012
C	219	+·00007	208	+·00003
U	227	+·00008	218	+·00010
C	239	+·00012	221	+·00003
U	244	+·00005	230	+·00009
C	257	+·00013	235	+·00005
U	261	+·00004	245	+·00010
C	270	+·00009	251	+·00006
U	272	+·00002	270	+·00019
C	278	+·00006	288	+·00018
U	278	......		
C	295	+·00017	Wire broke.	
	Wire broke.			

XXII. *On some Thermal and Volume Changes attending Mixture.* By FREDERICK GUTHRIE*.

[The paragraphs are numbered in sequence with those of my previous communications on Salt-Solutions and Attached Water.]

§ 256. It may be taken as a rule that solid crystalloids are more soluble in liquids when the two are at a higher than when at a lower temperature. The apparent exceptions to this rule are all, I believe, referable to the decomposition by heat which the solids undergo and the inferior solubility of the new products in the liquid.

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* Read November 8, 1884.

In §§ 238–241 *a* it was shown that the liquids triethylamine and water are remarkably more miscible when cooler than when warmer; and their relationship in this respect was pretty fully made out. The conclusion come to in this particular case was that, when the two liquids are brought together, a subcryohydrate is formed, and the heat attending (set free during) its formation may or may not be sufficient to effect its almost complete decomposition, or, rather, mitigate its formation according as the initial temperature of the two liquids is higher or lower. And that subsequent elevation of temperature affects decomposition. Depression of temperature promotes the formation of the subcryohydrate.

A liquid is in a different predicament from a solid when the question turns upon the solubility in a liquid medium. With a solid, increase of temperature always tends in the direction of fusion *per se*, which implies diminished cohesion and the bringing of the two (solid and liquid) into a community of physical state. In the case of two liquids, although, as before, rise of temperature may promote solution by diminishing cohesion, such promotion may be more than counterbalanced by the tendency of the increased heat to separate one or other liquid as a vapour, the particles of which, coalescing, form a liquid insoluble in the rest.

Be this as it may, it will be found that the separation of liquids from their mixtures by increase of temperature is by no means uncommon, and may be the rule rather than the exception long before temperatures approaching the critical ones are reached.

§ 257. *Change of Volume of Triethylamine and Water at about the Temperature of their Separation.*—The remarkable separation which takes place between triethylamine and water when a mixture of the two is warmed, and which was described in § 238, suggests the possible use of such a mixture as a calorimeter. For, if such separation is accompanied by any great change in volume, since the amount of additional heat required to effect a large separation is exceedingly small, a very exact measure of the heat given to the mixture by a given mass of matter cooling through a given range of temperature would be obtained by measuring such change of volume.

I accordingly took a bulb with a capillary stem and determined its capacity up to a lower mark on the stem, and then calibrated the stem. The capacity at 16°·1 was 9·1823 cubic centim. The mean volume of 1 millim. of the stem was ·000830038 cubic centim., or 0·00009039 of the capacity of the bulb. Into this bulb 5·4873 grams of water were introduced and then 3·0600 grams of triethylamine, making a 35·8-per-cent. solution. The two on being mixed and brought to the temperature of 16°·1 had a volume which may be called V, and which was 9·1820 cubic centim. The bulb was now kept for an hour at each 0°·5 higher temperature. In the following Table the rise in millimetres for every 0°·5 is given; such rise being corrected for the calibration of the tube and corrected also for the expansion of the glass (cubic expansion ·000026 for 1° C). The nearest tenths of millimetres only are given.

TABLE LVIII.

T.	Corrected increase on previous volume.	Corrected increase on original volume.	T.	Corrected increase on previous volume.	Corrected increase on original volume.
°	millim.	millim.	°	millim.	millim.
16·1	...	...	21·6	18·8	172·5
16·6	7·9	7·9	22·1	18·0	190·5
17·1	7·9	15·8	22·6	17·5	207·0
17·6	7·9	23·7	23·1	17·0	224·0
18·1	8·4	32·1	23·6	17·3	241·0
18·6	15·5	47·6	24·1	17·2	258·2
19·1	24·5	72·1	24·6	17·2	275·4
19·6	24·6	96·7	25·1	17·2	292·6
20·1	20·8	117·5	25·6	17·1	309·7
20·6	18·6	136·1	26·1	17·1	325·8
21·1	17·6	153·7	26·6	17·1	343·9

The original volume at 16°·1 being 9·1820 cubic centim., at, for example, 19°·1 it was 9·182 + 72·1 × ·00083001 *, or 9·2418 cubic centim. As the volumes in the third column are corrected for calibre, they serve at once to explain the behaviour of the liquid.

From § 237 it seems that the liquid here dealt with is, at starting, at 16°·1 a mixture of the subcryohydrate and the base itself. This mixture expands regularly from 16°·1 to 17°·6. Through that range equal increments of temperature are accompanied by equal expansions. At 18°·1 the liquid

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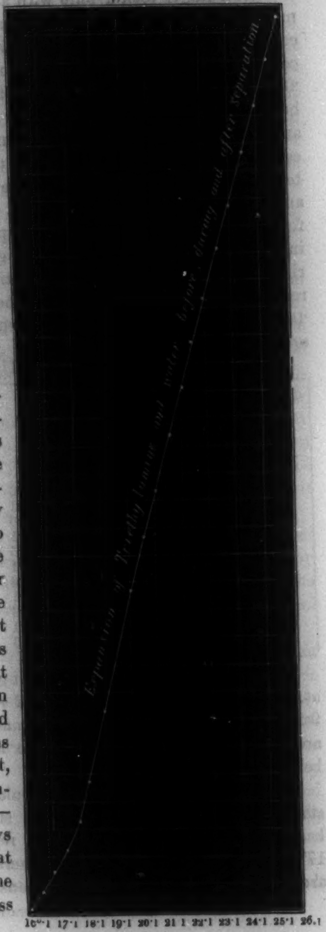
* From table of calibration.

Fig. 1.



is opalescent, and that opalescence is accompanied by an increased expansion. At 18°·6 the liquid becomes quite milky, and on standing separates into two of nearly the same density and refractive index. These two are about equal in volume (see § 241 *a*). The two next half-degree warmings produce a still greater separation; I mean that the total actual sinking of the watery solution and the rise of the ammoniacal solution is probably greater in this case than before. The joint expansion has increased. Now this may be brought about by two causes: either that the separation is greater, or that after separation the mean expansion by heat of the separated parts together is greater. That the increased expansion is not due to the second of these causes seems proved by the fact that, as the heating is continued, the expansion—although, indeed, always greater than that at temperatures below the separating point—is less than the expansion during separation. Separation produces some expansion ; and this being superadded to the expansion due to the increased temperature of the separated constituents gives rise to the elegant curve of fig. 1. The lower and upper parts of this curve are straight lines at different inclinations to the axis. The region of separation is indicated by a curve tangent to both, and whose mean tangent is more inclined than either to the axis of percentage.

Although, therefore, the separation of the mixed liquids into two immiscible liquids (each of which is mixed) is accompanied by an abnormal volume-change (increase), this increase is not so much larger than the increase attributable to mere heat-dilatation as to make the liquid even at the brink of its critical condition especially valuable as a calorimeter.

Another resource would be of course to measure the degree of separation approximately by measuring the height of the plane of separation of the two immiscible mixed liquids heated by a known mass cooling through a known range. This would be indeed in theory a very effective calorimeter; but I do not see the way at present to overcome certain practical difficulties of arrangement and manipulation.

§ 258. *Diethylamine and Water.*—These two liquids appear to mix in all proportions at all atmospheric temperatures above 0° C. An aqueous solution of the base, when heated in an open vessel, gives off the base as a vapour, and the temperature does not rise above 100° C.

Into a strong glass tube, which was afterwards sealed, was introduced a mixture consisting of 45·42 per cent. of diethylamine and 54·58 per cent. of water. On heating this in an oil-bath, with a thermometer, very gradually, and again letting the temperature fall slowly, the bath being kept well stirred, the following changes were observed :—

At 130° the liquid was still quite clear.
134°·5 separation was incipient.
135°. The lower layer amounted to about $\frac{1}{5}$ of the whole.
136°. " " " $\frac{1}{4}$ "
140°. " " " $\frac{2}{7}$ "
145°. " " " $\frac{1}{3}$ "
150°. " " " $\frac{1}{3}$ "
160°. " " " $\frac{1}{3}$ "

The conditions were not such as to allow of exact measurement. The critical temperature is, however, trustworthy; and the result shows that, within a range of about 10° C. only, the separation begins and is completed, as far as the completion is faithfully measured by the height of the plane of demarcation. It is to be noted that, owing in part to the refractive index of diethylamine being nearer that of water than is the refractive index of triethylamine, the above separation is not marked by the milkiness which characterizes the separation of the latter body *. If it were not for accidental dust-particles floating on the surface of the lower liquid it would be, in some cases, almost impossible to distinguish the two layers. As the phenomenon of separation is one which has to be watched for, the tubes cannot be enclosed in metal cases for the purpose of equalizing the pressure on the glass. Although only one tube of this series has burst, I have not cared to carry the temperature above 180° C., which must correspond to a pressure of about 15 atmospheres.

TABLE LIX.

Separation between Diethylamine and Water as Liquids.

Diethylamine per cent.	Water per cent.	Temperature at which separation begins.
12·64	87·36	Still clear at .... 180°.
15·02	84·98	Begins to separate at 128°.
16·30	83·70	„ „ 121·8.
20·94	79·06	„ „ 121.
26·89	73·11	„ „ 123.
37·80	62·20	„ „ 128.
45·42	54·58	„ „ 134·5.
62·35	37·65	„ „ 154.
75·76	24·24	Still clear at .... 170 (burst about 180°).

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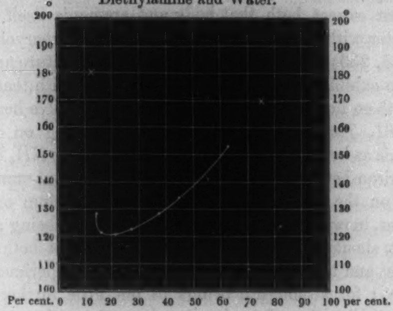
* Mr. Illingworth, a student in my physical laboratory, has been kind enough to determine the refractive indices of this group.

	ρ
Ethylamine	1·3718
Diethylamine....	1·3850
Triethylamine ..	1·3999

The determinations were made at 17° C., a temperature rather perilously near the boiling-point of ethylamine.

Fig. 2.

Diethylamine and Water.



A few points are noticeable in these experiments. The 12·64-per-cent. solution showed no true separation at 180°. On standing to cool, with the point of the tube a little above the oil, a layer was formed on the liquid surface of about 1 millim. in thickness. This layer subsisted even when the temperature of the bath had sunk to 100°, provided the tube was not shaken. On repeating the experiment, and removing the tube from the bath at 180°, it became evident that the phenomenon was one of distillation. The upper and partly empty end of the tube being the first to cool, the liquid of highest vapour-tension, namely the diethylamine, distilled into that region, condensed, and floated on the heavier and more aqueous portion. Such a layer is rather apt to be overlooked, but its growth may be watched in comfort after the temperature has fairly begun to sink.

§ 259. It should also be remarked that while a 12·64-per-cent. solution at 180° has only a slight etching-action on glass, the 62·35-per-cent. solution caused the surface of the glass (soft German) to peal off in visible scales when heated to 150°–160°, acting like a caustic alkali. This may be the reason of the bursting of the 75·76-per-cent. tube, which had a wall-thickness of 2·5 millim. and an internal diameter of 9 millim. It is well to remember, therefore, that a tube which has withstood a pressure due to a certain temperature may afterwards give way when even at a lower one.

§ 260. I have not succeeded in separating ethylamine from water by heat in closed vessels. But by the closest analogy we must expect both that body and ammonia itself to leave the water with which they are combined as subcryohydrates (§§ 235, 233); and at some very high temperature and pressure to exhibit nearly complete insolubility with that liquid. All of these liquids contract with water and evolve heat.

§ 261. *Tetrethylammonium Oxide.*—Looking on aqueous ammonia as being a solution in water of the oxide NH_4HO, the comparison between ethyl-, diethyl-, and triethyl-ammonium oxides on the one hand, and tetrethyl-ammonium oxide on the other, in regard to their solubilities in water being affected by heat, should present many points of interest both to the physicist and to the chemist. The following experiment may be noted; for although it brings us but little further in the immediate direction of our inquiry, it confirms the statement that a solution of tetrethylammonium is decomposed on concentration by evaporation. A 10-per-cent. solution heated in an oil-bath to 180° gives off a permanent gas which ultimately may burst the tube. This is no doubt olefiant gas. At the same time oily drops which float are formed in the tube; on cooling, they disappear. This is evidently triethylamine containing water; the reaction being

$$(C_2H_5)_4, NHO = (C_2H_5)_3, HNHO + C_2H_4.$$

And it appears that this known decomposition is brought about by heat alone without concentration.

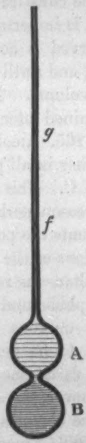
§ 262. *Tetramethylammonium Oxide* (a 10-per-cent. solution) does not show any separation at 200°, but begins to solidify at $-16°$. The tetrethyl compound of the same strength also solidifies in an ice-salt cryogen.

§ 263. *Ethylic Ether* may be here mentioned as a liquid which, though only slightly soluble in water, forms with it a solution decomposable by heat. Water saturated with ether at a given temperature, and heated in a closed tube a few degrees, becomes visibly milky. When such a solution is heated to 100° C., the ether, probably nearly anhydrous, forms a distinct layer on the top. It is redissolved on cooling. Now in § 104 it was shown that ether united with water. In § 274 it will be shown that such union is accompanied by the liberation of heat and by contraction. Here we have the third term of such relationship, namely, the decomposition of the combination by a rise of temperature.

§ 264. *Alcohol and Bisulphide of Carbon.*—It may be recalled that in §§ 207–228 strong, almost perfect, analogies were established between water-salt alloys and salt-salt alloys. So, now, I am led to consider the case of the mixture of two liquids neither of which is water. And in choosing for my first experiments alcohol and bisulphide of carbon, I was guided by the fact that, speaking from a chemical point of view, we should not expect there to be any relationship, and because both liquids can be got in a state of very great purity. The alcohol was obtained by distilling the nominally "absolute" from quicklime. The bisulphide was washed with water and distilled from oil of vitriol. A preliminary experiment showed that expansion resulted on mixing the two. A quill-tube about 4 feet long was closed at one end and half filled with the bisulphide; about an equal volume of alcohol was added. The tube was closed and the contents mixed. When the whole had resumed the air-temperature, a permanent lengthening of the column of about 11 millim. had taken place.

For exact determination the following method was employed. Two bulbs, A and B, nearly equal, were blown on a piece of thermometer-tubing of rather large bore (about 1 millim. internal diameter), the neck between the bulbs having the same width and being as short as practicable; the bulbs being weighed, bisulphide was introduced through a very fine capillary tube, until the lower bulb was filled at 17°·6. The whole was again weighed. The upper bulb and the lower part of the stem being filled with alcohol, the height *f* was noted at which the liquid stood at 17°·6. A third weighing followed. On tilting and frequently inverting, the two could be perfectly mixed. When brought again to 17°·6, the height *g* was observed. The volume of the capillary from

Fig. 3.



f to *g* is got by measuring the length, and weighing a column of mercury which has a length (exactly measured) of about the length *f–g*.

Actual weight of bisulphide . .	1·8180 gram.
„ „ alcohol . . .	1·9856 „
Reduced expansion (at 17°·6) .	0·02912 cub. cent.

This gives an expansion of 0·007405 of the original joint volume. The method is seen to be one capable of extreme accuracy, and is, I think, though more laborious, preferable to a specific-gravity method, because the temperature is better under control. This individual result has, however, no special numerical significance, because the two liquids are not in any simple relationship by weight or volume, and because, as we should expect and as we shall see is the case (§ 271), the ratio of change of volume depends upon the ratio of the constituents.

It is important to note that the increase in volume here observed is accompanied by a fall in temperature, which at first, and until the temperature is recovered, tends to reduce the volume. This, the natural corollary of expansion, will be examined later.

§ 265. Alcohol and bisulphide of carbon mix with one another in all proportions at all temperatures between 0° and 100° C. This fact does not seem to be generally known, the reason perhaps being that a very small quantity of water prevents the perfect mixture taking place between some proportions of the nominal constituents. The examination of the simultaneous reciprocal solubilities of the three bodies alcohol, bisulphide, and water would be a fascinating inquiry, but a very onerous one; for many thousand experiments would have to be performed in order to trace the effect of even a few variations in temperature and in the threefold ratio. Moreover, the complication would be much further increased by the chemical attitude between alcohol and water.

§ 266. I made nine mixtures of alcohol and bisulphide containing the two liquids in different ratios. The liquids were weighed in tubes closed at one end, and having capillary necks, which were then sealed off. These solutions, when used, were transferred to open tubes, which were then cooled in an ordinary ice-salt cryogen with the following results.

TABLE LX.

Separation of Alcohol and Bisulphide of Carbon by Cold.

Per cent. of bisulphide.	Per cent. of alcohol.	Temperature at which separation begins.
94·94	5·06	Remains clear down to −18°·4.
89·54	10·46	Becomes turbid at ......−14°·4.
84·89	15·11	„ „ ......−15°·9.
79·96	20·04	„ „ ......−16°·1.
65·11	34·89	„ „ ......−17°·7.
59·58	40·42	Remains clear down to −20°.
49·91	50·09	
39·96	60·04	
29·92	70·08	

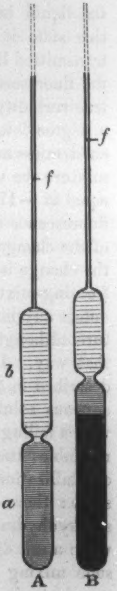
In these experiments, as the thermometer sinks it is noticed that at several degrees above that at which separation begins the liquid becomes opalescent, or rather fluorescent; for in this state it is still perfectly transparent, and colours the transmitted light of a light orange-yellow. It is pale blue by the fluoresced light. On reaching the critical temperature of true turbidity, the change is abrupt. At only the fraction of a degree lower the liquid divides into two with surprising suddenness and precision. In the case of the 79·96-per-cent. mixture the volumes of the two separated liquids are about equal at −17°, although at −15° only the above-mentioned fluorescence betrays the impending change. The suddenness of the change argues that the quantity of heat lost during the change is inconsiderable. Again, on removing from the freezing-mixture and shaking up, I have not been able to detect anything like a stationary thermometer during remixture, although all analogy shows that there must be a tendency that way. Indeed the phenomenon closely resembles that described in §§ 238–241*a* attending the decomposition of an aqueous solution of triethylamine. But it is here presented with a falling thermometer, there with a rising one. Here it resembles the separation of a solid salt containing water of crystallization from an aqueous solution which still retains some: there it was due to the decomposition by heat of a subcryohydrate. Here the original mixing absorbed heat, as when a salt dissolves in water: there it liberated heat. Here such mixing gained volume: there it lost volume. The one case is, as it were, a real image of the other, and inverted, because real.

Only such a little bit of this behaviour is revealed by an ice-salt cryogen that it would be almost useless to draw its curve from these four points. Laid out in percentages of alcohol from left to right, it seems as though its shape would be like that of the reflexion in the axis of percentages of the curve of diethylamine and water (fig. 2).

Alcohol, Bisulphide of Carbon, Amylene, Ether, Chloroform, and Benzol.

§ 267. Perhaps we may take the relationship between alcohol and bisulphide of carbon as being typical of such a relationship as resembles the solution of nitre in water, or of fused nitre in fused nitrate of sodium (§ 220) (which results in expansion of the solidified alloy), or, lastly, the solubility of fused nitre in water under pressure (§ 252). The method of experimenting adopted reveals, however, somewhat unexpected relationships between other liquids, which relationships are of a more chemical character. Many chemists have of late years made great use of the term "saturation," and the expression has been of some real service. But its unguarded use has, I venture to say, given rise to some misconception. The word itself certainly conveys something absolute and complete; and it is undoubtedly intended to convey such an idea, especially when prefixed by "perfect" or contrasted with "partial." It is only necessary to revert to the types of physical saturation upon which the analogies of chemical saturation are based, to show that such condition is relative and not absolute. Chemical saturation is not a remote analogue of electric neutrality, and the latter is clearly relative.

Fig. 4.



§ 268. Two or three tubes were made, similar in principle to that of fig. 3, but of more general use (fig. 4). In one of these the lower and upper bulbs (up to a subsequently marked point on the stem) were of absolutely the same capacity (between 3 and 4 cub. cent.). In the second the lower bulb was several times as big as the upper. By adding weighed quantities of mercury to the lower bulb, the ratio of contents could be changed at will.

In order to give an idea of the absolute and relative dimensions, I may state that in one of the tubes the exact capacity of *a* and *bf* at 17°·6 was 3·3777 c. c., the total volume upon which the expansion or contraction took place being therefore 6·7554 c. c. The mean volume of 1 millim. of the capillary tube about *f* was 0·00140183 c. c.; so that 1 millim. on the capillary meant 0·00020737 of the joint liquid volumes. As the readings could be made by means of a cathetometer* to within 0·2 millim., I imagine that the numerical results are strict to the fifth decimal place. The only other sources of error appear to be the mixing of the liquids during the filling of the upper bulb and capillary. The filling of both bulbs is effected by means of a funnel-capillary, which reaches about half way down into the bulb which has to be filled. Accidental soiling of the tube is removed by a thin German-silver cotton-covered wire.

In the following Table equal volumes at 17°·6 of the liquids enumerated were taken. There is in every case an expansion marked +, or a contraction marked −. Before these signs is H, C, or according as heat is liberated or absorbed. Immediately beneath these signs is the amount of contraction upon one volume of the original liquids taken jointly (before mixture). Below these is the temperature to which the altered volume has to be brought in order to restore it to the original (joint) volume.

The experimental errors appear here to be entirely due to (1) the diffusion during the second filling of the two liquids against gravity, an operation which lasts about 15 minutes, and (2) the imperfect purity of the substances. The first of these is quite negligible, as the common surface is only about 1 square millimetre, while the volumes are over 3 cubic centimetres.

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* Designed and made by the "Cambridge Scientific Instrument Company."

TABLE LXI.

Equal Volumes at 17°·6.

	Alcohol.	Ether.	Bisulphide of Carbon.	Amylene.	Chloroform.	Benzol.
Alcohol	0	H− ·006894 23°·5	C+ ·007278 11°	?	H− ·002488 19°·75	C+ ·0002488 17°·42
Ether	......	0	C+ ·001556 16°·5	H− ·0004977 18°·1	H− ·0108869 25°·8	H− ·00346308 20°·4
Bisulphide of Carbon......	......	......	0	C+ ·00311055 15°·05	C+ ·00688468 11°·7	C+ ·0069469 11°·1
Amylene ...	......	......	.. ...	0	H− ·0015138 19°·1	C+ ·0010783 16°·6
Chloroform .	......	......	......	......	0	C+ ·00183969 15°9
Benzol	......	......	......	......	......	0

In taking the tube out of its bath it is tilted, bulb upwards, so as to be at an angle of about 45°. Where the differences of refractive index and of density are great, complete mixture seems to be reached in five or six reversals of a few minutes each *. But in none of the cases given above were the reversals less than 20 in number nor of less duration than 10 minutes each, nor was the manipulation stopped before trial showed that constancy of volume had been reached. Each experiment from first to last takes about five hours. The open end of the capillary may be stopped by a short piece of caoutchouc-tubing containing a glass plug.

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* In making such experiments as these, the question presents itself—If two colourless (or similarly coloured) liquids have the same refractive index, how shall we know whether they are mixed or not? And if, therewith, they have the same density, how does their emulsion differ at all from their mixture? It is, indeed, unlikely that any two liquids have the same refractive indices or the same density at more than one temperature. And that they should have both refractive index and density alike at more than one temperature involves an improbability of a higher order. Apart from this, however, it is likely that the skin of a liquid has a different (higher) density and a higher refractive index than the mass of the same liquid. (F. G., Phil. Mag. November 1883.)

§ 269. Returning to Table LXI., a cloud of ideas suggest themselves. The results are obtained on equal volumes at an arbitrary temperature 17°·6 both before and after mixture. Wherever there is gain of volume, there is absorption of heat, cold, diminished heat-tension (C). Wherever there is loss of volume, there is liberation of heat, heating, increased heat-tension (H). These thermal effects are only given qualitatively in the Table, and were actually obtained in a second series of experiments made as follows. Equal volumes of the two liquids were run from burettes into two test-tubes of thin glass, one of about twice the capacity of the other. The narrower was put inside the wider, and both put into water at 17°·6. After sufficient standing, a thermometer in the inner liquid marks nearly the same temperature. The tubes are removed from the water and wiped, the inner one broken through at the bottom and used as a stirrer.

Let us consider, now, two of these cases more exactly, in one of which there is heat and contraction, in the other cold and expansion.

Ether and Chloroform.

Maximum Rise of Temperature.

§ 270. The liquids were weighed instead of being measured; otherwise they were treated as in § 269, with the exception that two experiments were made in each case; in the second experiment the thermometer-bulb was brought to the temperature shown in the first experiment before being used.

TABLE LXII.

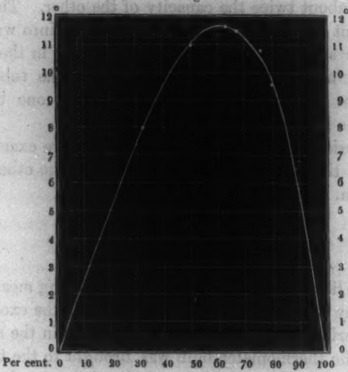
Showing Rise of Temperature from 17°·6 on mixing Ether and Chloroform in different proportions by weight.

Ether.	Chloroform.		Rise in temperature.
		Per. cent.	°
2	1	or 33·33	8·0
1	1	„ 50·00	11·0
1	1·615	„ 61·8	11·7 ($C_4H_{10}O : CHCl_3$)
1	2	„ 66·66	11·5
1	3	„ 75·00	10·9
1	4	„ 80·00	9·6

As we are here merely searching for a maximum, we may neglect certain effects which would be of the utmost importance under other circumstances. Thus the specific heat of none of the liquids is the same, and each rise of temperature given is weighted with the specific heat of the liquid in which it takes place. But I believe I am right in assuming that this effect would not in this instance materially shift the place of the maximum, although it would alter every one of the individual numbers, and that not in the same proportion.

The curve, fig. 5, shows the relationship of increased heat-tension to the proportions of chloroform and ether by weight by which it is caused.

Fig. 5.



From these six experiments, therefore, we find that the greatest change (rise) of temperature takes place when the liquids are in the proportion of 1 ether to 1·615 of chloroform by weight, which is the proportion of $C_4H_{10}O$ to $CHCl_3$.

§ 271. This method of experimentation, however, does not allow of such great accuracy as the method of change of volume. If it be found that the greatest change of volume takes place when these weight-ratios (1 ether to 1·615 of chloroform) are mixed, and that a very small change of ratio either way diminishes the change of volume, this evidence will be much strengthened towards the conclusion that the relationship is indeed between molecule and molecule.

Taking, therefore, the tube like A (fig. 3), having equal bulbs of 3·2325 c. c., I put 9·304 grams of mercury into the lower bulb. This reduced the capacity of the lower bulb 0·693 c. c., bringing it to 2·5390, the upper bulb by 3·2325. They are in the ratio of 1·380 to 1·084, which, again, are in the ratio of the molecular volumes (molecular weights divided by specific gravities) of the two liquids. The ratio-value of the capacity of the calibrated capillary-stem has now, of course, to be taken upon a lesser total volume—namely, upon 5·7715 instead of upon 6·4650. The first quantities of chloroform added should be shaken and warmed with the mercury, so as to displace the film of air between the mercury and the glass, or some dissolved gas. If this is not done before the ether is added, air-bubbles arise when the two are mixed, and vitiate the readings.

The result for equimolecular volume at 17°·6 is 0·0116756: chloroform 1, ether 1·2731.

Instead of 9·304, I now introduced only 9·0 grams of mercury; this reduced the lower bulb 2·5699 c. c., and the two together to 5·8024; the volume-ratio between the two being 1 chloroform to 1·258 ether. The shrinkage on the new volume was 0·0114783.

Next I introduced 9·6 grams of mercury. This reduced the lower bulb to 2·5241 c. c., and the two together to 5·7566. The volume-ratio between the two is now 1 chloroform to 1·2806 ether. The shrinkage on the new volume was 0·015706.

TABLE LXIII.

VOLUMES.		On being mixed and brought to the same temperature (17°·6) which they had before mixture, shrink to the below-given fraction of the joint volume they had before mixture.
Chloroform.	Ether.	
Per cent.	Per cent.	
50·00	50·00	·0108869
44·29	55·71	·0114783
43·99	56·01	·0116756 ($C_4H_{10}O$, $CHCl_3$)
43·83	56·17	·0115706

The table shows the great accuracy of which this method is capable, and discovers a maximum contraction exceedingly close to, if not at, the monomolecular ratio ; thus confirming the result got by the cruder method of increased heat-tension, § 270.

The liquid solidifies to a white crystalline mass at a constant temperature below 0°, which I shall give when I have determined it exactly.

It seems, then, that ether and chloroform unite chemically with one another to form the body $C_4H_{10}O$, $CHCl_3$, a substance which may be analogous in its composition with $S_2Cl_4\,2(C_4H_{10}O)$.

Vapour-tension of Chloroform and Ether Mixtures.

§ 272. The result of the experiments given above will make it imperative to revise previous ideas about the vapour-tension of mixed liquids. The following experiments with ether and chloroform show how the vapour-tension varies with the composition. The absolutely pure and dry substances were mixed in various proportions by weight, and each mixture was introduced into one of a series of perfect barometers in a room of uniform temperature. The barometers stood in the same trough close together. The readings were made with a cathetometer at a distance of nine feet. The readings were made backwards and forwards through the series three times. The atmospheric pressure was made constant by adjusting the mercury in the trough. About five grams of the liquid were introduced into each tube, and in all cases enough, as shown by a rough measurement and calculation, to ensure there being far more than sufficient of each kind of liquid to supersaturate. After determining the mercurial depression, the liquid columns above the mercury were measured, and their specific gravities assumed to be those due to mixture without change of volume. This is not quite true (see § 268). Further, it is assumed that the liquid has the same composition before as after its introduction into the tube. This, also, is not quite exact. Neither of these errors has been taken into account in the following Table ; for they are both of them negligible in comparison with the numerical data sought.

TABLE LXIV.

Vapour-tensions of Mixtures of Chloroform and Ether.

T=19°·02.

Chloroform, per cent. by weight.	Ether, per cent. by weight.	Mercurial depression.	Liquid above mercury.	Vapour-tension in millim of mercury at 19°·02.
100	0	200·0	84·0	190·7
90	10	205·2	87·2	196·0
80	20	222·3	106·5	211·7
70	30	236·2	104·0	226·4
63	37	240·2	79·2	233·1
($C_4H_{10}O$, $CHCl_3$) 61·76	38·24	243·9	85·0	236·4
60	40	248·5	81·2	241·4
50	50	285·0	83·3	278·2
40	60	318·7	85·2	312·2
30	70	349·8	77·5	344·8
20	80	383·2	81·8	377·9
10	90	413·8	83·9	408·8
0	100	442·6	90·0	437·8

§ 273. The increase of vapour-tension as the proportion of ether increases is therefore continuous, but by no means regular. There is in the neighbourhood of the monomolecular ratio a diminution in the rate of increase; but immediately this region is past, the curve becomes rectilinear. As the barometer-tubes stand side by side in a row, they present a very interesting appearance, as the mercurial levels form a curve closely similar to that in fig. 6, A (p. 271) turned upside down. Guided by heat-development and shrinkage, we have therefore detected the existence of $C_4H_{10}O$, $CHCl_3$, and showed that the vapour-tension confirmed the existence of this body. Are we, then, to assume that in every case in Table LXI. where there is heat-development and shrinkage, there is also true chemical union? Reluctant as some may be to admit to the title of chemical compounds a class of bodies which probably numbers many thousands, there seems no help for it. There can be but little doubt, for instance, that ether unites with alcohol and benzol, that chloroform unites with alcohol and with amylene, and so on. The experiments necessary for the proof of this assertion will be laborious, and will require such care and concentration that I must again invite other workers into this fertile field. There is, however, one point which may be here noted. Two elements may unite to complete saturation in respect of one another, yet the molecules so formed may be quite prepared to unite as a whole with another atom or molecule (compare § 267).

§ 274. The contraction and heating attending the mixing of alcohol and water have been long known. When, in § 98, I described the solid combination of the two, $C_2H_6O, 4H_2O$, and called it a cryohydrate (I should now call it a subcryohydrate), I did not suppose that it was only one of so numerous a family as appears to be the case. In § 104 was briefly described a combination of ether with water. I may here mention the circumstance that equal volumes of the two, when shaken together at 17°·1, rise in temperature to 18°·9. Equal volumes brought together at 17°·6 in the experimental tube of § 268, and agitated by a globule of mercury being made to pass to and fro through the capillary opening, contract 0·005436 of their joint volume, and require to be heated to regain that volume. This contraction is probably very far from the maximum, as there is no doubt a large quantity of passive matter present. For the same reason, the maximum liberation of heat will probably be found with a less water-ratio. Where the maximum heat-liberation occurs we should look for the subcryohydrate, and there also for the maximum contraction.

Vapour-tensions of Mixtures of Bisulphide of Carbon and Ether.

§ 275. Taking next an instance where expansion and cold result from mixture, I give at once the numerical results as to the vapour-tensions of the various mixtures.

TABLE LXV.

Vapour-tensions of Mixtures of Bisulphide of Carbon and Ether.

T=18°·88 C.

Bisulphide of Carbon, per cent. by weight.	Ether, per cent. by weight.	Mercurial depression, in millim.	Liquid above mercury, in millim.	Vapour-tension, in millim. of mercury, at 19°·02.
100	0	291·9	78·1	284·5
90	10	353·3	77·5	346·3
80	20	380·8	75·0	374·3
70	30	404·1	82·8	387·3
60	40	416·5	81·2	410·1
50	50	425·2	80·0	419·3
40	60	441·0	90·9	424·6
30	70	434·8	75·0	429·8
20	80	438·1	83·4	433·0
10	90	437·2	81·7	432·5
0	100	436·5	81·7	432·1

Specific gravity of ether, 0·72 ; of bisulphide of carbon, 1·23.

§ 276. Laid out graphically we get accordingly the curve B, fig. 6. Perhaps the most notable character of this curve is its descent at the upper right end. This means that, although bisulphide of carbon has a lower vapour-tension than ether, a little bisulphide loosens the ether and raises the vapour-tension. The effect on the vapour-tension of the liquid brought about by the addition of a little ether to the bisulphide is much more marked.

Vapour-tensions of Mixtures of Chloroform and Bisulphide of Carbon.

§ 277. Referring again to Table LXI. it is seen that, with whatever of the liquids there examined bisulphide of carbon is mixed, expansion occurs and the temperature is lowered. With chloroform these results are very marked; and having examined the relationship between bisulphide and ether and between chloroform and ether, let me describe the relationship between chloroform and bisulphide of carbon.

TABLE LXVI. *a*.

Vapour-tensions of Mixtures of Chloroform and Bisulphide of Carbon. T=16°·0 C.

Chloroform, per cent. by weight.	Bisulphide of Carbon, per cent. by weight.	Mercurial depression, in millim.	Liquid above mercury, in millim.	Vapour-tension, in millim. of mercury, at 16°.
0	100	269·9	53·1	264·8
3	97	271·8	58·2	266·2
5	95	277·5	74·9	270·4
10	90	271·6	57·8	266·1
15	85	272·3	56·2	266·8
20	80	273·0	61·9	266·9
30	70	270·7	70·7	263·7
40	60	265·8	60·2	259·7
50	50	260·3	61·3	254·0
60	40	249·6	56·0	243·7
70	30	241·0	60·0	234·6
80	20	227·9	60·5	221·4
90	10	215·4	80·8	206·6
100	0	176·2	64·6	169·2

Spec. grav. of bisulphide of carbon, 1·23; of chloroform, 1·49.

§ 278. On laying these numbers out graphically, the curve C, fig. 6, presents itself. Although we are dealing here with millimetres, the shape of the curve towards pure bisulphide of carbon required confirmation. I therefore employed a temperature of nearly 2° C. lower; and having prepared fresh examples of the liquids with equal care, and having changed the barometer-tubes, I found:—

TABLE LXVI. *b*.

Vapour-tensions of Mixtures of Chloroform and Bisulphide of Carbon. T=13°·8 C.

Chloroform, per cent. by weight.	Bisulphide of Carbon, per cent. by weight.	Mercurial depression, in millim.	Liquid above mercury, in millim.	Vapour-tension, in millim. of mercury, at 13°·8.
0	100	259·5	83·0	251·6
5	95	266·0	108·1	255·7
10	90	260·3	91·0	251·5
15	85	258·5	85·2	250·3
20	80	255·5	70·9	248·6
30	70	252·5	70·9	245·4
40	60	248·0	73·3	240·6
50	50	243·5	83·0	235·0
60	40	236·1	78·2	227·8
70	30	220·3	59·5	214·0
80	20	210·7	76·5	202·3
90	10	199·1	78·1	190·4
100	0	170·0	113·2	158·4

Spec. grav. of bisulphide of carbon, 1·23; of chloroform, 1·49.

Fig. 6.

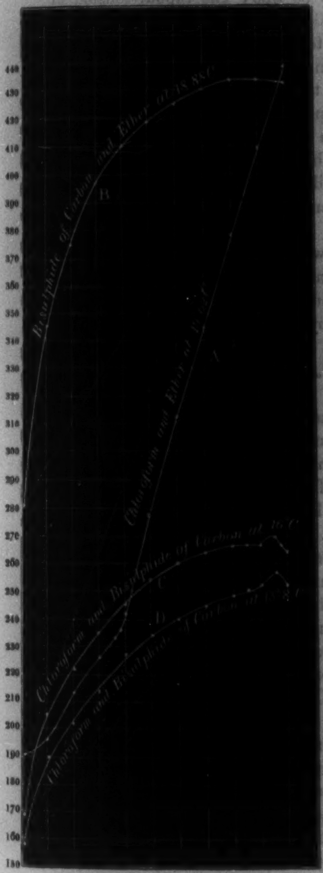
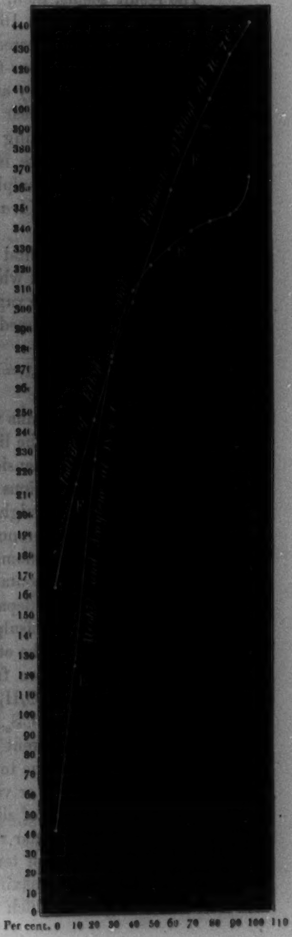

Bisulphide of Carbon and Ether at 18.8°C
B
Chloroform and Ether at 18.8°C
A
Chloroform and Bisulphide of Carbon at 16°C
C
Chloroform and Bisulphide of Carbon at 18.8°C
D
440
430
420
410
400
390
380
370
360
350
340
330
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150

Fig. 7.


E
F
440
430
420
410
400
390
380
370
360
350
340
330
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Per cent. 0 10 20 30 40 50 60 70 80 90 100 110

The result seems, then, to be this: The vapour-tension of bisulphide of carbon at 16°·0 is 264·8 millim., at 13°·8 it is 251·6 millim., both referred to mercury at those temperatures. Of chloroform the vapour-tensions at these two temperatures, also referred to mercury at the same temperature, are 169·2 and 158·4. A very great increase of the vapour-tension is brought about by mixing a very little bisulphide with the chloroform; a little rise is brought about by mixing a little chloroform with the bisulphide. The graphic interpretations of the two Tables LXVI. *a* and LXVI. *b* are shown in curves C and D, fig. 6.

§ 279. If we could find two liquids showing neither contraction nor expansion when mixed, and neither liberating nor absorbing heat, the vapour-tension of a mixture of such liquids should be expressed by the equation

$$vt_{(ma+nb)} = vt_a + \frac{ma(vt_b - vt_a)}{ma+nb},$$

where generally vt_s means the vapour-tension of the liquid s, and where a and b are the liquids and m and n their respective masses. The vapour-tension curve would be a straight line joining the vapour-tensions of the constituents. The maximum departure from this straight line on the curves in fig. 6 gives us the maximum interference. This, in the case of chloroform and ether, is at the monomolecular ratio. Now, if we search the curve of mixtures containing bisulphide of carbon, we find there also a maximum departure from the mean at a certain ratio. In the case of bisulphide of carbon and ether this is at 30 or 35 per cent. of the ether (say 32·5). This implies that the maximum departure from the mean takes place where 1 molecule of ether ($C_4H_{10}O$) is mixed with 2·02 molecules (say 2 molecules) of CS_2. At this ratio we may suppose there to be no indifferent or inert matter. If we consider chemical union to be due to an action of attraction, and regard the maximum thermal or volume effects as taking place when there is no superfluity of either constituent, so here we have an equally distinct molecular ratio, and an absolutely definite one (at all events at a given temperature), where a sort of anti-union takes place—a maximum effect of repulsion. This is a state of things for which some new nomenclature may be necessary. There may be as many anticombinations as there are combinations; and the former may be quite as definite in weight-ratio as the latter. The essential difference is that, while attraction may result in the production of new stuffs, the latter has the locally opposite action.

Again, with chloroform and bisulphide the maximum departure from the mean is at 40 per cent. bisulphide. This signifies 1 molecule chloroform to 1·05 molecule bisulphide. I therefore submit these formulæ—

$$C_4H_{10}O \longleftrightarrow 2CS_2,$$

$$CHCl_3 \longleftrightarrow CS_2.$$

What is the relative nature of the bodies which should give a straight line on the vapour-tension curve of their various mixtures? Such may probably be found amongst hydrocarbons. I find that when equal volumes of ethylic and amylic alcohols are mixed at 13°·9, the temperature rises to 15°·1, implying the formation of a species of double alcohol. Referring to Table LXI. (§ 268) and to the few representative bodies there considered, we find that amylene and alcohol are almost without volume-change.

An examination of the vapour-tensions of their mixtures gave the following numbers :—

TABLE LXVII.

Alcohol, per cent.	Amylene, per cent.	Mercury.	L. C.	Sp. gr.	Correction.	V.-T.
100	0	46·2	73	·79	4·3	41·9
90	10	129·8	99	·78	5·7	124·1
80	20	232·2	85	·76	4·8	227·4
70	30	282·1	85	·75	4·8	277·3
60	40	313·9	90	·73	4·9	309·0
50	50	329·0	98	·72	5·3	323·7
40	60	335·3	101	·71	5·3	330·0
30	70	339·6	100	·69	5·1	334·5
20	80	340·7	117	·68	5·9	334·8
10	90	344·1	121	·67	6·0	338·1
0	100	362·0	112	·66	5·5	356·5

T=18°·4 C. Spec. grav. of alcohol, ·79; of amylene, ·66.

The curve is seen in fig. 7, E (p. 271).

Through the favour of my colleague, Dr. Hodgkinson, I obtained some pure iodide and bromide of ethyl. These were again washed, dried, and redistilled. The following Table shows the vapour-tensions of their mixtures. They were shielded from the light when in contact with the mercury.

Table LXVIII.

Iodide of ethyl.	Bromide of ethyl.	Mercury.	L. C.	Sp. gr.	Correction.	V.-T.
0	100	459	65	1·40	6·8	452·2
10	90	439	100	1·45	10·8	428·2
20	80	415	88	1·50	9·8	405·2
30	70	389	74	1·55	8·6	380·4
40	60	372	93	1·60	11·1	360·9
50	50	343	87	1·65	10·7	332·3
60	40	316	76	1·70	9·6	306·4
70	30	286	73	1·75	9·6	276·4
80	20	260	98	1·80	13·1	246·9
90	10	227	88	1·85	12·2	214·8
100	0	172	62	1·90	8·8	163·2

T=16°·7 C. Spec. grav. of bromide, 1·4 ; of iodide, 1·9.

The curve F, fig. 7, shows that the vapour-tensions of the mixtures of these two substances lie nearly in a straight line, and that the two substances therefore very closely fulfil the condition of absolute non-interference.

PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

JANUARY 1885.

XXIII. *On the Determination of Chemical Affinity in terms of Electromotive Force.*—Part IX.

By C. R. ALDER WRIGHT, *D.Sc.* (*Lond.*), *F.R.S.*, *Lecturer on Chemistry and Physics, and* C. THOMPSON, *F.C.S.*, *Demonstrator of Chemistry, in St. Mary's Hospital Medical School*[*].

On Voltaic and Thermovoltaic Constants.

164. THE experiments described in Part VIII.[†] show that the difference in E.M.F. between two two-fluid cells containing metallic salts in solution, and alike in all respects save that one of the fluids is of different degrees of concentration in the two cells respectively, can be readily obtained by opposing the two cells to one another, and measuring the current set up through a total resistance large enough to reduce the current to such an extent that its density, in reference to the plate-surfaces in the cells, falls below a certain limiting value variable with the details of the construction of the cells; and, further, that the same value is obtained by means of "diffusion-cells," consisting of two vessels containing respectively the two solutions of different degrees of concentration but containing the same salt, united

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[*] Read November 8, 1884.

[†] *Ante*, p. 78.

by a siphon-tube, or constituting a "gravity" arrangement. If a be the increment in E.M.F. thus measured, due to a given increase in the strength of the fluid surrounding the plate acquiring the higher potential, and b be the corresponding decrement[*] due to a given increase in strength of the other fluid, then E and e, the electromotive forces of the cell when containing the two stronger and the two weaker fluids respectively, are related so that, within experimental-error limits,

$$E = e + a - b.$$

It follows from this fact, and from the circumstance that in many cases the values of a and b are considerable fractions of e, that the great majority of the valuations hitherto made and published of the electromotive forces of various two-fluid cells cannot be properly compared with the heat-evolutions due to the net chemical actions taking place in the cells; because no accurate valuations having been made of the strengths of the solutions used, and the precise character of the plate-surfaces employed not having been noted, the values of the terms a and b cannot be calculated with precision so as to enable the values of E to be deduced for some given standard-strength of solution (*e. g.* for strength MSO_4 $100H_2O$, or MCl_2 $100H_2O$, &c.). Differences of several centivolts, and even decivolts, exist between the values assigned to certain voltaic combinations by different observers, mainly due to this cause. Accordingly it becomes necessary to repeat most of the work of previous experimenters with due regard to these points before comparisons can be satisfactorily instituted. A large number of cells have therefore been examined during the last four years, under strictly comparable conditions, in order to obtain sufficiently accurate values for the purpose of tracing out the correlations subsisting in different cases between the heat-evolution due to the net chemical change and the maximum E.M.F. actually developed, when so small a current flows as to cause no appreciable diminution by "polarization."

All these observations completely confirm the conclusions already arrived at, that *Volta's law of summation holds* within the limits of experimental error, and that *the effect of a given alteration in the molecular strength of a saline solution surrounding one of the plates of a two-fluid cell is sensibly independent of the nature of the other fluid and the other plate.* It hence becomes possible to assign numerical values or constants to given metals immersed in solutions of their salts of given nature and strength, such that the E.M.F. of a voltaic combination formed by combining two such immersed metals (by allowing the two solutions to interdiffuse, *e. g.* in a Raoult cell or in a "gravity" cell) is calculable by taking the difference between the constants ; *i. e.* by employing the formula

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[*] With cells set up with acid fluids (*e. g.* dilute sulphuric acid) surrounding the plate acquiring the lower potential, increasing the strength of the acid fluid not infrequently causes an increment, and not a decrement, in the E M.F. of the combination; *e. g.* in Daniell cells (§§ 112-114, Part V.).

$$E = C_1 - C_2,$$

where E is the E.M.F. of the combination, and C_1 and C_2 the two constants involved, such that if $C_1 - C_2$ is of + sign the metal to which C_1 applies acquires the higher potential, whilst if $C_1 - C_2$ is of − sign the metal to which C_2 applies acquires the higher potential. For instance, if C_2 apply to zinc and C_1 to copper in sulphate solution, $C_1 - C_2 = +1{\cdot}114$, and copper acquires the higher potential ; whilst if C_1 refer to magnesium, $C_1 - C_2 = -{\cdot}725$, and zinc acquires the higher potential.

165. The value of the *voltaic constant* thus applicable to any given metal is variable, within certain limits, with its surface-conditions (according as bright fused metal, electro-deposited, amalgamated, &c.), and also with the nature and strength of the solution of its salt in which it is immersed, and probably also with the temperature, but is independent of the nature of the other half of the cell. In order to fix the numerical value some convention must be made as regards the zero to be adopted as starting-point. For this purpose, and in view of the comparisons desired to be instituted between the values of $C_1 - C_2$ and the heat-evolutions due to the net chemical actions taking place, the most convenient assumption appears to be this :—that the potential of an amalgamated zinc plate immersed in a solution of a given salt of zinc of given molecular strength is assumed to be zero, for the purpose of fixing the numerical value of the potential of a plate of the metal to be examined *when immersed in an equally strong solution of the corresponding salt of that metal,* the two solutions being allowed to interdiffuse (*e. g.* in a "gravity" cell or in a "Raoult"

cell). For instance, when plates of electro-copper or cadmium are respectively immersed in solutions of the sulphates of these metals, and opposed to amalgamated zinc immersed in zinc-sulphate solution, the molecular strength throughout being $1{\cdot}0\,MSO_4\ 100\,H_2O$, the potentials of the copper and cadmium plates are respectively $+1{\cdot}114$ and $+{\cdot}360$ volt higher than the potential of the zinc plate; which values are accordingly the "voltaic constants" for electro-copper in $1{\cdot}0\,CuSO_4\ 100\,H_2O$, and for electro-cadmium in $1{\cdot}0\,CdSO_4\ 100\,H_2O$ respectively: whence it results that the E.M.F. of a cell set up with electro-copper and electro-cadmium plates and solutions of the sulphates of these metals of molecular strength $1{\cdot}0\,MSO_4\ 100\,H_2O$ will be

$$E=C_1-C_2=1{\cdot}114-{\cdot}360={\cdot}754,$$

which in point of fact is the case. On the other hand, when magnesium is opposed in the same way to zinc in sulphate solutions of strength $1{\cdot}0\,MSO_4\ 100\,H_2O$, the former metal acquires a potential lower by ·725 volt than that of the latter; whence it results that $-{\cdot}725$ is the voltaic constant for magnesium in sulphate solution of this strength; wherefore the potential difference set up between magnesium and copper in sulphate solutions of this strength will be $1{\cdot}114-(-{\cdot}725)=1{\cdot}839$ volt, which in practice is found to be the case. Evidently Volta's law of summation is involved in the proposition that the E.M.F. of a voltaic combination is the algebraic difference between the values of the voltaic constants as thus defined.

If the value of a given voltaic constant applying to a given metal immersed in a solution of one of its salts of given strength be known, that for any other given strength is readily calculable by means of the formula $E=e+a-b$ when tables of the values of a and b are extant, like those given in Part VIII. for certain kinds of plate-surfaces in chloride and sulphate solutions.

Out of a large number of voltaic combinations examined, consisting of two metals immersed in solutions of their salts of a given kind (*e. g.* sulphates, chlorides, nitrates, or acetates), only a few have been found to possess an E.M.F. which, when at its maximum, differs by but little from the value calculated from the heat-evolution during the net chemical action taking place in the cell, *i. e.* from the difference between the heats of formation of the two salt solutions forming the electrolytes; the great majority either fall short of this value, or exceed it by quantities well outside of the limits of experimental error. In cells of the latter class, it is evident that the extra work which can be done by the passage of a current through a large external resistance over and above that due to the net chemical change, must be accomplished by a transformation of sensible heat into electric energy; *i. e.* it is done at the expense of sensible heat, such cells resembling in this respect various of the diffusion-cells described in Part VIII. A still more remarkable class of cells has been found, however, in which the current flows in the direction *opposite* to that deducible from the relative heats of formation of the electrolytes, so that, instead of the plate immersed in the solution of the salt of greater heat of formation acquiring the lower potential (as the zinc plate in a Daniell cell), it actually acquires the higher potential. The passage of a current in such cases, consequently, is accompanied by a twofold transformation of sensible heat into current energy, actual or potential; for the chemical changes that take place in the cell are accompanied on the whole by heat-absorption, whilst any work done externally must be performed at the expense of sensible heat*. Twenty such combinations have been examined, *vide* § 209.

166. An attentive consideration of these and other allied phenomena leads to the conclusions that, since only in exceptional cases does the formula hold,

$$E_H = E = C_1 - C_2$$

(where E_H is the E.M.F. corresponding to the net heat-evolution due to chemical change in the cell), *the E.M.F. actually generated must be due to other causes in addition to the heat of chemical change*; and that all the observed phenomena may be clearly accounted for if it be assumed that the difference of potential set up between the two plates of the voltaic combinations examined *is due to the superposition of two causes*—one, the net heat-development or difference in heat of formation of the two electrolytes surrounding the two plates respectively; the other, an action akin to that taking place in a thermoelectric combination, and, like that action, expressible numerically by the algebraic difference between two constants applicable to the two halves of the combination respectively; so that if k_1 and k_2 be the two *thermovoltaic* constants applicable respectively to the metals (and corresponding with the voltaic constants C_1 and C_2), and E_H be the E.M.F. corresponding with the difference between these heats of formation, then

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* A somewhat analogous phenomenon is presented by gravity-diffusion cells set up with platinum plates and nitric acid of different degrees of concentration. With certain strengths an E.M.F. is set up superior to that calculable from the heat of intermixture of the two acid fluids; so that when a current flows through a large external resistance, part of the work done is performed at the expense of sensible heat; whilst the passage of the current reduces the concentrated acid to lower oxides of nitrogen (precisely as in a Grove's cell), thereby absorbing additional heat.

$$E = C_1 - C_2 = E_H + k_1 - k_2.$$

If, then, $k_1 - k_2$ does not differ greatly from zero, E and E_H are nearly equal; if, on the other hand, $k_1 - k_2$ has a considerable value, E exceeds or falls short of E_H according as that value is positive or negative in sign. If $k_1 - k_2$ is negative in sign and also is numerically greater than E_H, E is of the opposite sign to E_H. This case corresponds with the class of cells above referred to in which the metal actually acquiring the higher potential is the one which would be expected to acquire the lower one, were the heat of chemical action the sole cause of potential difference in the cell.

The value of the thermovoltaic constant applicable to any given metal necessarily varies in the same way as that of the voltaic constant; *i. e.* it is to some extent dependent on the nature of the metal surface, and varies with the nature and strength of the solution of the salt of the metal employed to surround the plate, and probably also with the temperature*.

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* S. Czapski has recently found (*Annalen der Physik*, xxi. p. 209) that zinc-silver-chloride and cadmium-silver-chloride cells diminish in E.M.F. as the temperature rises; whilst iron-mercurous-chloride, cadmium-mercurous-chloride, and zinc-mercurous-bromide cells rise in E.M.F. with increasing temperature. In the former class of cell the E.M.F. actually set up is less, and in the latter greater, than that corresponding with the heat-evolution due to the net chemical change. But it would seem that if there be any general law connecting the variations in E.M.F. with temperature, it is less simple than might appear from these particular

In some few cases the constant is of positive sign for some solution-strengths or kinds of salts, and negative for others: in these cases the numerical value of the thermovoltaic constant is never great, not exceeding a few centivolts at most. If, on the other hand, a metal possess a thermovoltaic constant of considerable magnitude for one class of salts, the sign is the same for all classes of salts examined. So that practically metals may be divided into three classes, viz.:—those where the thermovoltaic constant has uniformly a more or less considerable negative value, *e. g.* lead and silver; those where the value is sometimes positive and sometimes negative but never large, *e. g.* copper and cadmium; and those where the value is considerable and always positive, *e. g.* iron, mercury, magnesium, and aluminium.

In order to have a standard for reduction, it is convenient to make the same convention as that above referred to for voltaic constants, viz. that the thermovoltaic constant for amalgamated zinc is taken as zero *when immersed in a solution of a zinc-salt corresponding in nature and molecular strength with the solution of the salt surrounding the other plate.*

As regards the actual numerical values assigned below to the voltaic and thermovoltaic constants, it has been thought best to adhere to the same fundamental assumptions as have been hitherto made throughout this series of papers, viz.:—that the B.A. unit of resistance is actually one earth-quadrant per second; that the factor for converting gramme-degrees into volts is 4410; and that the E.M.F. of Clark's cell at 15°·5 is 1·457 volt, that of a Daniell cell set up with amalgamated-zinc and electro-copper plates and solutions of zinc and copper sulphates of equal molecular strength being $\cdot 765 \times 1\cdot 457 \pm \cdot 0005$, or $1\cdot 114 \pm \cdot 0005$ volt. The present state of our knowledge would introduce corrections in all three of these values; but these corrections would so far balance one another that the most probable end result is that all the numerical values given are about 1·6 to 2·2 per cent. too high. First, the true value of the B.A. unit is about 1·3 per cent. lower

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results; for Clark's cells (zinc-mercurous-sulphate) obviously belong to the same class as zinc-mercurous-bromide and cadmium-mercurous-chloride cells; and yet the E.M.F. of a Clark's cell *falls* instead of rising as the temperature rises (§§ 139 and 179).

than that thus assumed; next, Lord Rayleigh's recent valuations of the E.M.F. of Clark's cell indicate 1·434 instead of 1·457, or 1·6 per cent. lower (this correction including the previous one). Still smaller values, 1·427 to 1·433 volt, or from 1·7 to 2·1 per cent. lower than Clark's value, have recently been obtained by Von Ettingshausen (*Zeitsch. für Electrotechnik*, 1884, Heft xvi.); whilst, lastly, the value of JF, the factor for converting heat units into volts, as deduced from the most recent experiments of Mascart, Kohlrausch, and Lord Rayleigh, is nearly as much below 4410; these three observers finding for the C.G.S. electrochemical equivalent of silver respectively the values ·01124, ·011183, and between ·01118 and ·01119, from which a mean value of close to ·0112 results; so that $F = \frac{\cdot 0112}{107\cdot 93} = \cdot 0001038$; whence, taking $J = 41\cdot 55 \times 10^6$, it follows that $JF = 4313$, or 2·2 per cent. below 4410. So that, on the whole, both E and E_H are uniformly overvalued below by amounts probably amounting to between 1·6 and 2·2 per cent.; whence their differences will evidently be overvalued to sensibly the same extent. The errors thus introduced into the values assigned to the various thermovoltaic constants calculated are in no case of such magnitude as to interfere with the general character of the inferences drawn from the numbers thus deduced.

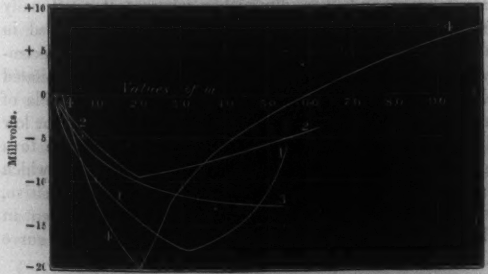
167. A number of cells have been examined, in which a sparingly soluble electrolyte was employed in the form of the solid salt suspended in a solution of some other salt (usually the one surrounding the other plate), *e.g.* zinc-silver-chloride cells, where the silver plate was surrounded by a magma of silver chloride suspended in zinc-chloride solution; or cadmium-lead-sulphate cells, where lead sulphate suspended in cadmium-sulphate solution surrounded the lead plate. Some noteworthy peculiarities have been observed with such cells as regards the fluctuations in the values of a and b in the formula $E = e + a - b$ with variations in solution-strength. Thus, with zinc-lead-sulphate cells (set up with a magma of lead-sulphate and zinc-sulphate solution round the lead plate) the effect of variation in the strength of the zinc-sulphate solution surrounding the lead plate is not the same, either in magnitude or sign, as the effect of the same variation in the

strength of the zinc-sulphate solution surrounding the zinc plate. In the latter case (as already shown, Part VIII.) the effect is of this kind, that as the solution-strength increases the numerical value of *b* continually increases, its sign being always the same, viz. positive; but in the former case this is not so, the numerical value of *a* increasing with the strength of the zinc-sulphate solution in which the lead sulphate is suspended up to a certain strength, after which the value again decreases, the sign being *negative* throughout. Thus the following Table represents the relative values of *a* and *b* for solution-strengths $m\text{ZnSO}_4\ 100\ \text{H}_2\text{O}$, the values of *b* being those described in § 153 for amalgamated-zinc plates, and those of *a* similarly obtained by means of a series of diffusion-cells set up with electro-coated lead plates immersed in magmas of recently precipitated well-washed lead-sulphate and zinc-sulphate solutions of varying strengths; the values are given in millivolts.

Value of *m*.	*a*.	*b*.
·1	0	0
·5	− 6·0	+11·1
1·0	− 9·5	+16·3
2·0	−14·0	+22·6
3·0	−18·0	+27·7
4·0	−16·5	+33·9
5·0	−11·0	+39·5
5·5	− 5·5	+43·5

Curve no. 1, fig. 1, indicates these values of *a* as ordinates, the values of *m* being abscissæ.

Fig. 1.



On substituting solutions of cadmium sulphate for those of zinc sulphate as the menstrua in which to suspend lead sulphate in cells containing lead and its sulphate as one half of the element, analogous results were obtained as regards the general character of the curve, the mean numerical values of *a* obtained by means of diffusion-cells being given in millivolts in the following Table, and represented by curve no. 2; the third column in the table and curve no. 3 represent the corresponding values obtained with diffusion-cells containing mercurous sulphate suspended in zinc-sulphate solutions of varying strengths, the plate-surfaces being in this case pure mercury (the "plates" being the upper surfaces of mercury occupying the lowest portions of the vessels constituting the cells).

Values of *m*.	Values of *a* in cells containing lead sulphate suspended in $m\text{CdSO}_4$ 100 H_2O.	Values of *a* in cells containing mercurous sulphate suspended in $m\text{ZnSO}_4$ 100 H_2O.
·1	0	0
·5	−2·3	− 5·0
1·0	−5·2	− 6·6
2·0	−9·2	− 9·5
3·0	−8·1	−11·6
4·0	−6·9	−12·2
5·0	−5·6	−12·7
5·5	−5·0	−13·0
6·0	−4·3	

It is here evident that whilst the sign of *a* is in all cases negative, the numerical value attains a maximum in the case of lead sulphate suspended in either zinc- or cadmium-sulphate solution and then diminishes, whereas it continually increases in the case of mercurous sulphate suspended in zinc sulphate. On the other hand, cells containing electro-silver plates immersed in magmas of recently precipitated well-washed silver chloride and solutions of zinc chloride of varying strengths, gave values for *a* negative in sign for low solution-strengths, and increasing in numerical value to a negative maximum as the strength increased, after which the value diminished again to 0, finally becoming positive, and increasing continuously; these values are given in millivolts in the following table, and indicated by curve no. 4.

Value of m.	Value of a in cells containing silver chloride suspended in $m\mathrm{ZnCl}_2$ 100 H_2O.
·25	0
·5	− 5·0
1·0	−12·0
2·0	−20·1
3·0	−10·2
6·0	+ 0·1
10·0	+ 7·0

Analogous values were obtained with cells containing mercurous chloride suspended in zinc-chloride solution, a being negative in sign with strengths where $m < 6·0$, but positive where $m = 10·0$.

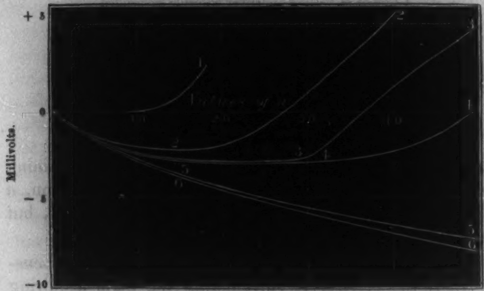
168. It is evident that cells of the type now under discussion, where the electrolyte surrounding the plate acquiring the higher potential is of a mixed character (*i. e.* containing two salts), are to a certain extent comparable with Daniell cells in which the copper plate is surrounded by a mixed solution of zinc and copper sulphates, the only essential difference being in the greater solubility of copper sulphate as compared with lead sulphate, &c. It seemed of interest, therefore, to examine in detail the influence on the numerical value of the E.M.F. of a Daniell cell exerted by addition of zinc sulphate to the copper-sulphate solution used. Accordingly a number of cells were set up containing mixed sulphate solutions of strengths $m\mathrm{CuSO}_4, n\mathrm{ZnSO}_4$ 100 H_2O, the values of m and n varying in the different cases, but all else being the same. The following remarkable results were thus obtained, electro-copper plates being used throughout:—

1. With solutions such that m constantly $= 1·77$, the value of a with continually increasing values of n is never negative, being sensibly $= 0$ as long as n does not exceed ·5, and being +, and continually increasing in numerical value as n increases above ·5.

2. With solutions such that m does not exceed ·5, the value of a is always negative, increasing in numerical value as n increases.

3. With solutions such that $m =$ from 1·0 to 1·42, the value of a is at first negative, increasing to a negative maximum as n increases, then diminishing to zero, and finally becoming positive, and continuously increasing in numerical value.

Fig. 2.



The following Tables represent these results, which are also indicated by curves 1 to 6 (fig. 2); the values are given in millivolts.

Value of $m=1{\cdot}77$. (Curve No. 1.)

Value of *n*.	E.M.F. of cell.	Value of *a*.
0	1114·0	
·1	1114·0	0
·5	1114·0	0
1·0	1114·1	+ ·1
1·5	1114·7	+ ·7
2·0	1117·9	+3·9

$m=1{\cdot}42$. (Curve No. 2.)

Value of *n*.	E.M.F. of cell.	Value of *a*.
0	1114·0	
·5	1112·6	−1·4
1·0	1112·0	−2·0
1·5	1111·9	−2·1
2·0	1112·1	−1·9
3·0	1115·0	+1·0
4·0	1119·5	+5·5

$m=1{\cdot}28$. (Curve No. 3.)

Value of *n*.	E.M.F. of cell.	Value of *a*.
0	1114·0	
1·0	1111·8	−2·2
1·5	1111·0	−3·0
3·0	1110·9	−3·1
4·0	1115·2	+1·2
5·0	1118·7	+4·7

Table (*continued*).

$m=1{\cdot}00$. (Curve No. 4.)

Value of n.	E.M.F. of cell.	Value of a.
0	1114·0	
·25	1113·3	− ·7
·5	1112·6	−1·4
1·0	1111·7	−2·3
1·5	1111·0	−3·0
2·0	1110·9	−3·1
3·0	1110·8	−3·2
4·0	1111·9	−3·1
5·0	1114·2	+ ·2
$m={\cdot}5$. (Curve No. 5.)		
0	1114·0	
·1	1113·6	− ·4
·25	1113·3	− ·7
·5	1112·6	−1·4
1·0	1111·5	−2·5
2·0	1110·0	−4·0
4·0	1107·7	−6·3
5·0	1106·7	−7·3
$m={\cdot}25$. (Curve No. 6.)		
0	1114·0	
·25	1113·1	−0·9
1·0	1111·4	−2·6
3·0	1108·4	−5·6
5·0	1106·1	−7·9

Hence it appears that cells containing very sparingly soluble compounds like lead sulphate, silver chloride, &c., suspended in solutions of more soluble salts, are comparable with Daniell cells in which the copper plates are surrounded with solutions containing only small quantities of copper sulphate, together with varying quantities of zinc sulphate, increasing the strength of the solution of the more soluble salt, in the first case producing the same general effect on the E.M.F. of the cell as addition of more zinc sulphate to the copper-sulphate solution in the second.

169. A probable explanation of these results is the following:—The passage of a current, however feeble, decomposes both electrolytes in the mixed fluid simultaneously;

so that, for example, in the Daniell cell containing mixed zinc- and copper-sulphate solution round the copper plate, both zinc and copper would be thrown down simultaneously in the metallic state, were it not that whilst still nascent the zinc acts on the copper-sulphate solution by a secondary action, precipitating the equivalent amount of copper, and becoming itself zinc-sulphate solution. A portion of the energy gained by this secondary action is nonadjuvant, the amount of nonadjuvant energy depending, *inter alia*, on the number of molecules of zinc sulphate thus reproduced relatively to that of copper sulphate in solution, in such a fashion that *the stronger the copper-sulphate solution*, cæteris paribus, *the less is the amount of nonadjuvant energy.* Hence, from this cause the E.M.F. of a Daniell cell would be necessarily diminished by addition of zinc sulphate to the copper-sulphate solution. But this addition produces also an effect of another kind; for addition of zinc sulphate to the fluid surrounding the plate acquiring the higher potential, making that fluid stronger so far as zinc sulphate is concerned, must set up an interdiffusion effect which will be superposed upon the other sources of difference of potential, tending to raise the potential of the plate immersed in the fluid thus strengthened relatively to that of the other plate. Hence there are two causes, acting in opposite directions, thus brought into play, tending to affect the potential-difference set up between the two plates of the cell: if the one predominate, the E.M.F. of the cell as a whole is lowered; if the other predominate, the E.M.F. is raised. With weak solutions of copper sulphate the former tendency is always greater than the latter, and the E.M.F. falls continuously as zinc sulphate is added to the copper-sulphate solution, as indicated in curves nos. 5 and 6, fig. 2. With strong solutions of copper sulphate the latter tendency is always greater than the former, so that in this case the E.M.F. continuously increases in value as zinc sulphate is added to the copper sulphate, as indicated in curve no. 1. With intermediate strengths of copper-sulphate solution, the former tendency at first predominates over the latter one, the E.M.F. of the cell falling as more zinc sulphate is intermixed with the copper sulphate; but by and by the second tendency becomes stronger relatively to the first, and finally overpowers it, thus causing the E.M.F. of the cell first to cease diminishing, and then to rise continuously until it reaches and even surpasses the first value.

Mutatis mutandis, evidently the same kind of explanation applies in the case of cells where the mixed electrolyte is a magma of a sparingly soluble salt suspended in a solution of a more soluble one.

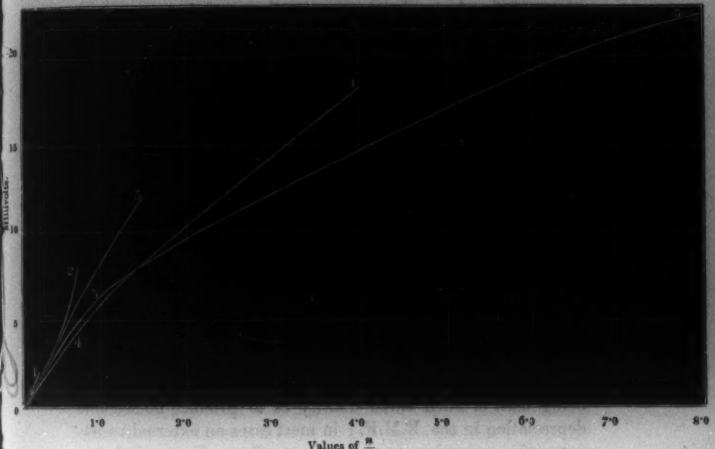
It should hence evidently result that the effect of "polarization" on cells set up with such magmas (*i. e.* the depreciation in E.M.F. observed with increasing current-density) should be much more marked than with cells containing only readily soluble salts in moderately concentrated solution; since the film of fluid surrounding the plate on which metal is deposited must, with such a magma, become very rapidly depreciated, as regards the amount in solution of the sparingly soluble salt, on account of the decomposition of that salt caused by the passage of the current. This is, in fact, the case, depreciation of some tenths of a millivolt being readily observable even with currents of density too small to produce any measurable effect on such diffusion-cells as those described in Part VIII. In order to avoid errors from this cause exceeding 0·5 millivolt in magnitude, it was found indispensable to work with currents of density not exceeding from ·01 to ·02 microampere per square centimetre when cells containing such magmas were employed; so that with plates exposing some 3 or 4 square centimetres of surface, and cells of near to 1 volt in E.M.F., a total resistance of at least a megohm, and usually of several megohms, was employed; and proportionately in other cases.

It should further result, if the above explanation be correct, that if two cells be compared, alike in all respects save that in one the copper plate is surrounded by a mixed solution $m\,CuSO_4$, $n\,ZnSO_4$ $100\,H_2O$, and in the other by a solution of copper sulphate only, of equal strength, viz. $(m+n)CuSO_4$ $100\,H_2O$, the difference between the E.M.F.'s of the two for a given value of the ratio $\frac{n}{m}$ will not be constant, but will increase as the value of m diminishes, *i. e.* as the mixed solution is weaker so far as the copper sulphate contained is concerned. This is in fact the case, as shown by the following Table, representing the E.M.F.'s of such pairs of cells uniformly containing amalgamated-zinc and electro-copper plates, the former immersed in $m\ ZnSO_4\ 100\ H_2O$; the E.M.F.'s of the cells containing $m\ CuSO_2$, $n\ ZnSO_4\ 100\ H_2O$ are derived from the preceding tables, and those of the cells containing $(m+n)CuSO_4\ 100\ H_2O$ are calculated by means of the formula $E=1114+a$, in which 1114 is the constant E.M.F. in millivolts of an ordinary Daniell cell containing $m\ MSO_4\ 100\ H_2O$, where m is constant for both zinc- and copper-sulphate solutions (§ 170, footnote), whilst a is derived from the table given in Part VIII. § 154.

m.	n.	E.M.F. of cells containing		Difference.	$\frac{n}{m}$.
		$(m+n)CuSO_4$ 100 H_2O.	$m\ CuSO_4$, $n\ ZnSO_4$ 100 H_2O.		
1·77	·5	1116·9	1114·0	2·9	·28
1·42	·5	1116·9	1112·6	4·3	·35
1·42	1·0	1120·2	1112·0	8·2	·70
1·00	·25	1115·6	1113·3	2·3	·25
1·00	·5	1117·2	1112·6	4·6	·50
1·00	1·0	1120·4	1111·7	8·7	1·0
1·00	1·5	1123·4	1111·0	12·4	1·5
·5	·1	1114·9	1113·6	1·3	·2
·5	·25	1116·3	1113·3	3·0	·5
·5	·5	1118·6	1112·6	6·0	1·0
·5	1·0	1121·8	1111·5	10·3	2·0
·5	1·5	1125·0	1110·7	14·3	3·0
·5	2·0	1128·0	1110·0	18·0	4·0
·25	·25	1119·6	1113·1	6·5	1·0
·25	1·0	1125·8	1111·4	14·4	4·0
·25	2·0	1132·1	1109·9	22·2	8·0

Fig. 3 represents these numbers, the values of $\frac{m}{n}$ being the abscissæ and those of the "differences" the ordinates of the curves drawn, which are evidently such that the curve where m has the highest value overlies the others; and similarly throughout.

Fig. 3.



Determination of the Numerical Values of the Voltaic Constants and Thermovoltaic Constants applicable to various kinds of Two-fluid Cells.

170. In all the cells examined, wherever possible, the plates used were coated over by an electro-deposited coat of metal, thrown down by a moderately weak current from a strong solution of a pure salt of the metal. The plates employed usually exposed a total surface of 3 or 4 square centimetres, and the electro-coating was effected by passing the current from three to five Leclanché quart-cells in series through a decomposing cell, in which the plate to be coated formed the negative electrode, the positive one being a plate of the same metal in as great a state of purity as practicable; the electrodes were usually some 3 or 4 centimetres apart. Under these circumstances the coating of metal formed was fairly tough and coherent, although in certain cases somewhat crystalline on the surface. Copper thus deposited from a strong solution of copper sulphate formed a coating of great

regularity and toughness. In some cases, however, bright plates of fused metal were necessarily employed, *e. g.* with iron and aluminium. With zinc the plates always consisted of pure metal superficially amalgamated with pure mercury. The cells employed were uniformly constructed of two small beakers or porcelain vessels containing respectively the metals and fluids employed, and united by a siphon-tube, consisting of an inverted Y-tube, the lower ends of which were covered over with thin animal membrane secured by a silk thread, and rendered watertight, when requisite, at the junction of the glass and membrane by the application of a little melted gutta-percha, so that no leakage into or from the siphon took place, saving by osmosis through the membrane. In all cases the temperature varied from 18° C. by only ± a few degrees. Saving in the case of certain experiments quoted from previous portions of these researches, and a few others made for special reasons with the quadrant-electrometer, all the observations were made by means of the galvanometer, currents being used of such small density as to produce no sensible depreciation in the E.M.F.; in most cases an external resistance of a megohm (and in many of much more) being employed, the valuation being obtained by comparing the readings of the cell to be examined with those of an Alder-Wright's normal Daniell cell * through the same resistance, using the formula

$$E = 1{\cdot}114 \times \frac{m}{n},$$

where m is the average reading of the cell to be valued, and

---

* The term "normal Daniell cell" has been applied by different observers to very different forms of cell, varying several per cents. in E.M.F. amongst themselves, principally according as sulphuric acid of one strength or another, or zinc-sulphate solution saturated or otherwise, is used to surround the zinc plate. What is here referred to as an "Alder-Wright's normal Daniell" is a cell set up after Raoult's form of construction, with amalgamated-pure-zinc and electro-copper plates immersed in pure solutions of their respective sulphates *of the same molecular strength*, preferably of strength $m\,MSO_4\ 100\ H_2O$, where m is near to 2·0, *i. e.* with copper-sulphate solution nearly but not absolutely saturated, so as not to deposit crystals by chilling or slight evaporation. The ratio of the E.M.F. of such a cell to that of a Clark's cell at 15°·5 has been found to be sensibly ·765 to unity.

n that of the standard Daniell. Usually alternate readings of the two cells were taken for 20–30 minutes after first setting up, and averaged to obtain the values of m and n.

A. *Voltaic and Thermovoltaic Constants of Metals immersed in Solutions of their Sulphates.*

I. *Copper.*

171. Electro-copper presents the remarkable and almost unique peculiarity, that the value of its voltaic constant in sulphate solution, as above defined, is practically uniform for all solution-strengths; for, as already shown, the E.M.F. of a zinc-copper-sulphate cell is sensibly the same whatever the solution-strength when amalgamated-zinc and electro-copper plates are used, viz. (on the assumptions above discussed, § 166) $1{\cdot}114 \pm {\cdot}0005$ volt; so that the voltaic constant for electro-copper in sulphate solution is sensibly $+1{\cdot}114$ for all solution-strengths (*i. e.* when referred to amalgamated zinc in zinc-sulphate solution of the same strength as zero).

The thermovoltaic constant of electro-copper also shows the same independence; for the experiments described in § 160 show that the heats of dilution of zinc- and copper-sulphate solutions are sensibly identical for equal dilution-ranges; hence the heats of formation of zinc- and copper-sulphate solutions both of strength $m\ MSO_4\ 100H_2O$ (where m is the same) must differ by a constant amount whatever the value of m: this amount for $m = {\cdot}25$ (and therefore for all other values of m) is, from Thomsen's results:—

$$\begin{array}{rr} \text{Zn, O, SO}_3\text{ aq.} = & 106090 \\ \text{Cu, O, SO}_3\text{ aq.} = & 55960 \\ \hline & 50130 = 1{\cdot}105 \text{ volt.} \end{array}$$

Hence, finally, since $E = 1{\cdot}114$ and $E_H = 1{\cdot}105$ for all solution-strengths, the thermovoltaic constant for electro-copper in sulphate solution is constantly $1{\cdot}114 - 1{\cdot}105 = +{\cdot}009$ for all solution-strengths.

II. *Cadmium.*

172. The experiments with the quadrant-electrometer described in Part VI. show that the electromotive forces of all

zinc-cadmium-sulphate cells set up with solutions of zinc and cadmium sulphate of the same strength, $m\ \mathrm{MSO_4}\ 100\mathrm{H_2O}$, are comprised within the limits $\cdot360 \pm \cdot0015$, when m is between ·08 and 2·0, and that those of the analogous copper-cadmium-sulphate cells are similarly comprised within the limits $\cdot7525 \pm \cdot0015$.

The experiments described in Part VIII., however, enable still more exact figures to be deduced. Applying the formula $E = e + a - b$, and taking the values of a and b from the tables quoted, the following figures result as the most probable ones, probable error in no case being so great as $\pm \cdot002$ volt:—

Value of m.	E.M.F. of zinc-cadmium cell.	E.M.F. of cadmium-copper cell.	Voltaic constant for electro-cadmium.
·1	·362	·752	+·362
·25	·362	·752	+·362
·5	·361	·753	+·361
1·0	·360	·754	+·360
2·0	·359	·755	+·359
3·0	·358		+·358
4·0	·3575		+·3575
5·0	·357		+·357

Unlike that of copper therefore, the voltaic constant for electro-cadmium immersed in $m\ \mathrm{CdSO_4}\ 100\mathrm{H_2O}$, referred to amalgamated zinc in zinc-sulphate solution of the same strength as zero, *varies with the value of* m, *decreasing as* m *increases.*

From these values the corresponding thermovoltaic constants are thus calculable. According to Julius Thomsen the heats of formation of zinc and cadmium sulphates in solution of strength $\cdot25\ \mathrm{MSO_4}\ 100\mathrm{H_2O}$ differ by 16210 :—

$$\begin{aligned} \mathrm{Zn, O, SO_3\ aq.} &= 106090 \\ \mathrm{Cd, O, SO_3\ aq.} &= 89880^{*} \\ \hline & 16210 \end{aligned}$$

The heats of dilution to this strength of more-concentrated

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[*] *Thermochemische Untersuchungen*, vol. iii. p. 285. In the calculations given in Part VI. the value 89500 is assigned, taken from Thomsen's earlier publications (*Journ. prakt. Chem.* xi. p. 401).

solutions are not equal in the two cases : calling them respectively h_1 and h_2, the heat of displacement per gramme-molecule of cadmium from $m\ \mathrm{CdSO_4}\ 100\mathrm{H_2O}$ by zinc is calculable by the formula

$$\mathrm{H} = 16210 - (h_1 - h_2);$$

when m, h_1, and h_2 have the following values :—

m.	h_1.	h_2.	$16210-(h_1-h_2)$.	Corresponding E.M.F.
·25	0	0	16210	·357
·5	0	25	16235	·358
1·0	0	75	16285	·359
2·0	50	275	16435	·362
3·0	100	450	16560	·365
4·0	175	625	16660	·367
5·0	375	825	16660	·367

Hence the values of the thermovoltaic constants for electro-cadmium immersed in $m\mathrm{CdSO_4}\ 100\mathrm{H_2O}$ (referred to amalgamated zinc immersed in equally strong zinc-sulphate solutions) *are positive for weak solution-strengths and negative for considerably strong solutions*, being in no case numerically great, viz. as follows :—

m.	E.	$\mathrm{E_H}$.	Thermovoltaic constant.
·25	·362	·357	+·005
·5	·361	·358	+·003
1·0	·360	·359	+·001
2·0	·359	·362	−.003
3·0	·358	·365	−·007
4·0	·3575	·367	−·0095
5·0	·357	·367	−·010

III. *Silver.*

173. The experiments already described in Part VI. show that the E.M.F.'s of zinc-silver-sulphate cells and the corresponding cadmium- and copper-silver cells are respectively 1·536, 1·1805, and ·4235, when amalgamated-zinc and electro-silver, -copper, and -cadmium plates are used with solutions of ·042 $\mathrm{MSO_4}$ 100 $\mathrm{H_2O}$ throughout. The probable error attaching to these values was in each case between ±·001 and

±·0015. Hence, referred to amalgamated zinc in zinc-sulphate solution of this strength as zero, the following values result for the voltaic constant of electro-silver in saturated silver-sulphate solution :—

From Zinc-Silver cells	1·536
From Cadmium-Silver + Zinc-Cadmium cells 1·1805 + ·362	=1·5425
From Copper-Silver + Zinc-Copper cells . . 1·114 + ·4235	=1·5375
Mean......	1·539

These three valuations do not accord so well as those obtained in most of the experiments subsequently detailed and made by means of the galvanometer ; the chief causes of the discrepancies lie in the greater want of permanence and wider range of fluctuation noticed with these cells (*vide* §§ 125–128, Part VI.), probably due to the extremely weak solutions necessarily employed owing to the sparing degree of solubility of silver sulphate.

Taking the mean value 1·539 volt as the voltaic constant for electro-silver in saturated silver-sulphate solution, it results that the corresponding thermovoltaic constant has a large negative value ; for Julius Thomsen finds that Ag_2, O, SO_3 aq. = 20390, whence the heat of displacement of silver from silver-sulphate solution by zinc is 85700 gramme-degrees = 1·890 volt, so that the thermovoltaic constant

$$k = E - E_H = 1\cdot539 - 1\cdot890 = -\cdot351.$$

IV. *Lead.*

174. A number of cells were examined set up with well-washed recently precipitated lead sulphate (prepared from clear lead-acetate solution and pure sulphuric acid in excess, boiled up many times with distilled water, and washed by decantation), suspended in zinc- or cadmium-sulphate solutions of varying strength. Electro-coated lead plates immersed in these magmas were opposed to amalgamated-zinc plates immersed in zinc-sulphate solution with the following results, to which are also joined the figures obtained with similar cells, in which electro-copper and electro-cadmium plates immersed in solutions of their sulphates respectively were opposed to the lead plates. The probable error of each value is in almost

every instance considerably below ±·001 volt, and in no case exceeds ±·002 volt. The values refer to cells containing on both sides solutions of the same molecular strength $m\,MSO_4\;100\,H_2O$.

m.	Lead sulphate suspended in zinc-sulphate solution.			Lead sulphate suspended in cadmium-sulphate solution.	
	Zinc-Lead.	Cadmium-Lead.	Lead-Copper.	Zinc-Lead.	Lead-Copper.
0·1	·537	·173	·577	·550	·564
0·5	·520	·160	·594	·537	·577
1·0	·512	·152	·603	·529	·585
2·0	·501	·142	·611	·519	·596
3·0	·491	·133		·514	
4·0	·487			·509	
5·0	·487			·505	
5·75	·487			·501	

From these various cell-values, together with those above described for zinc-copper and zinc-cadmium, the following valuations are deducible for the voltaic constants of electrolead immersed in a magma of lead sulphate in $m\,ZnSO_4\;100\,H_2O$, or in a magma of lead sulphate in $m\,CdSO_4\;100\,H_2O$.

Lead Sulphate suspended in Zinc-sulphate Solution.

m.	Zinc-Lead.	Zinc-Cadmium + Cadmium-Lead.	Zinc-Copper − Copper-Lead.	Mean.
0·1	·537	$\left.\begin{array}{r}\cdot173\\+\cdot362\end{array}\right\}=\cdot535$	$\left.\begin{array}{r}1\cdot114\\-\ \cdot577\end{array}\right\}=\cdot537$	·536
·5	·520	$\left.\begin{array}{r}\cdot160\\+\cdot361\end{array}\right\}=\cdot521$	$\left.\begin{array}{r}1\cdot114\\-\ \cdot594\end{array}\right\}=\cdot520$	·520
1·0	·512	$\left.\begin{array}{r}\cdot152\\+\cdot360\end{array}\right\}=\cdot512$	$\left.\begin{array}{r}1\cdot114\\-\ \cdot603\end{array}\right\}=\cdot511$	·512
2·0	·501	$\left.\begin{array}{r}\cdot142\\+\cdot359\end{array}\right\}=\cdot501$	$\left.\begin{array}{r}1\cdot114\\-\ \cdot611\end{array}\right\}=\cdot503$	·502
3·0	·491	$\left.\begin{array}{r}\cdot133\\+\cdot358\end{array}\right\}=\cdot491$		·491
4·0	·487			·487
5·0	·487			·487
5·75	·487			·487

Lead Sulphate suspended in Cadmium-sulphate Solution.

m.	Zinc-Lead.	Zinc-Copper — Copper-Lead.	Mean.
0·1	·550	1·114 − ·564 } = ·550	·550
0·5	·537	1·114 − ·577 } = ·537	·537
1·0	·529	1·114 − ·585 } = ·529	·529
2·0	·519	1·114 − ·596 } = ·518	·5185
3·0	·514		·514
4·0	·509		·509
5·0	·505		·505
5·75	·501		·501

From these mean values for the voltaic constants the following numbers are deduced as the thermovoltaic constants for electro-lead in contact with solid lead sulphate suspended in zinc- or cadmium-sulphate solution; the heat of displacement of lead from (solid) lead sulphate by zinc forming solution of zinc sulphate of strength m $ZnSO_4$ 100 H_2O being

$$106090-73800-h=32290-h;$$

where 106090 = Zn, O, SO_3 aq. (m = ·25),
73800 = Pb, O, SO_3 aq. (solid),
h = heat of dilution of m $ZnSO_4$ 100 H_2O to ·25 $ZnSO_4$ 100 H_2O (§ 160).

m.	*h.*	E_H.	Lead sulphate suspended in zinc sulphate.		Lead sulphate suspended in cadmium sulphate.	
			E.	$E-E_H$.	E.	$E-E_H$.
0·1	0	·712	·536	−·176	·550	−·162
0·5	0	·712	·520	−·192	·537	−·175
1·0	0	·712	·512	−·200	·529	−·183
2·0	50	·711	·502	−·209	·5185	−·1925
3·0	100	·710	·491	−·219	·514	−·196
4·0	175	·708	·487	−·221	·509	−·199
5·0	375	·704	·487	−·217	·505	−·199
5·75			·487		·501	

Hence electro-lead in connexion with its sulphate is analogous to silver, the thermovoltaic constant possessing a considerable *negative* value ; so that zinc-lead-sulphate and cadmium-lead-sulphate cells have E.M.F.'s notably below the values corresponding with the net chemical actions taking place therein. On the other hand, since the thermovoltaic constant for copper is a small positive value ($+\cdot009$ for all solution-strengths), and that for lead is in all cases a considerably larger negative value, whilst copper is the metal acquiring the higher potential in a lead-copper-sulphate cell, it follows that the value of $k_1 - k_2$ in such a cell is always a considerable + quantity, varying from $+\cdot009-(-\cdot162)$ to $+\cdot009-(-\cdot221)$; that is from $+\cdot171$ to $+\cdot230$, according as the lead sulphate is suspended in zinc- or cadmium-sulphate solution, and according as the molecular strength of the solutions is low or high. In other words, a lead-copper-sulphate cell gives an effective maximum E.M.F. of from ·171 to ·230 volt *above that corresponding with the net chemical action taking place therein.* This chemical action represents a heat-evolution of $73800-55960=17840$ gramme-degrees per gramme-molecule, corresponding with ·393 volt only. The actually observed values consequently correspond to an increment of about 50 per cent. in the E.M.F. of the cell above that due to chemical action.

On the other hand, since the thermovoltaic constant for silver in contact with saturated silver-sulphate solution is a negative quantity numerically greater than that for lead, whilst in lead-silver-sulphate cells silver is the metal acquiring the higher potential, the value of $k_1 - k_2$ in such cells must be negative. Thus a cell set up with electro-silver immersed in saturated silver-sulphate solution opposed to electro-lead immersed in a magma of lead sulphate suspended in ·042 $ZnSO_4$ 100 H_2O, must yield a value for $k_1 - k_2$ close to $-351-(-\cdot176)=-\cdot175$; that is, the E.M.F. of such a cell must be close to $1\cdot1775-\cdot175=1\cdot0025$ volt, since the heat of displacement of silver from silver-sulphate solution by lead forming solid lead sulphate is $73800-20390=53410$ gramme-degrees per gramme-molecule, equivalent to 1·1775 volt. On trying the experiment, the following values were observed with a number of similar cells :—

Maximum cell-value = 1·008 volt.
Minimum ,, = 1·001 ,,
Average ,, = 1·003 ,,
Probable error ± ·0008 ,,

the average observed value being thus sensibly identical with the calculated one.

V. *Iron.*

175. A number of cells were examined set up with electro-copper plates immersed in copper-sulphate solution, opposed to plates of brightened sheet iron of as high a degree of purity as could be obtained, immersed in freshly prepared ferrous-sulphate solution; and, similarly, numerous observations were made with analogous cells containing electro-cadmium plates immersed in cadmium-sulphate solution, amalgamated-zinc plates immersed in zinc-sulphate solution, or electro-lead plates immersed in a magma of lead sulphate suspended in zinc-sulphate solution. The following average values were obtained: with solutions of molecular strength throughout ·1 MSO_4 100 H_2O, the cells exhibited far greater want of permanence and much wider fluctuations in E.M.F. than were noticed with cells of strength 1·0 MSO_4 100 H_2O; so that, whilst the probable error in the former class of cells ranged from ±·003 to ±·005, that in the latter class was only from ±·001 to ±·002. The negative sign attached to the values for the iron-cadmium cells indicates that iron was the metal acquiring the higher potential, contrary to what might *à priori* be anticipated from the heats of formation, viz. Fe, O, SO_3 aq. = 93200 and Cd, O, SO_3 aq. = 89880 [*].

Pairs of metals.	Molecular strength 1·0 MSO_4 100 H_2O.	Molecular strength 0·1 MSO_4 100 H_2O.
Zinc-Iron	·399	·445
Iron-Cadmium	−·035	−·073
Iron-Lead	·112	·120
Iron-Copper	·715	·685

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[*] This peculiarity of iron-cadmium-sulphate cells has been already noticed by Braun (*Annalen der Physik*, xvi. p. 561).

These values, together with those above cited for zinc-cadmium, zinc-lead, and zinc-copper cells, give the following valuations for the voltaic constant for polished metallic iron in ferrous-sulphate solution :—

m.	Zinc-Iron.	Zinc-Cadmium—Cadmium-Iron.	Zinc-Lead—Lead-Iron.	Zinc-Copper—Copper-Iron.	Mean.
1·0	·399	$\left.\begin{matrix}\cdot360\\+\cdot035\end{matrix}\right\}\cdot395$	$\left.\begin{matrix}\cdot512\\-\cdot112\end{matrix}\right\}\cdot400$	$\left.\begin{matrix}1\cdot114\\-\cdot715\end{matrix}\right\}\cdot399$	·398
0·1	·445	$\left.\begin{matrix}\cdot362\\+\cdot073\end{matrix}\right\}\cdot435$	$\left.\begin{matrix}\cdot537\\-\cdot120\end{matrix}\right\}\cdot417$	$\left.\begin{matrix}1\cdot114\\-\cdot685\end{matrix}\right\}\cdot429$	·432

It results from these figures that the thermovoltaic constant for polished iron in ferrous-sulphate solutions must always have a notable positive value. Admitting, what is doubtless the case, that the heats of dilution of ferrous- and zinc-sulphate solutions from the molecular strengths 1·0 MSO_4 100 H_2O to 0·25 MSO_4 100 H_2O are not widely different, so that their difference is negligible, the heat of displacement of iron from 1·0 $FeSO_4$ 100 H_2O by zinc is $106090-93200=12890$ gramme-degrees per gramme-molecule, corresponding with ·284 volt. Since iron acquires the higher potential in zinc-iron-sulphate cells, the value of k_1-k_2 must be positive and $=\cdot398-\cdot284=+\cdot114$; whence the thermovoltaic constant for iron must be $+\cdot114$ for 1·0 $FeSO_4$ 100 H_2O; and must consequently have higher values still for weaker solutions, approximating to $\cdot432-\cdot284=+\cdot148$ volt for 0·1 $FeSO_4$ 100 H_2O.

Hence *iron is an example of a class of metals opposite in thermovoltaic power to silver and lead*, and differing from copper and cadmium in that, whilst with the last two metals the thermovoltaic constant has never a value largely above or below zero, with silver and lead it has considerable negative values, and with iron it has a notable positive value.

One result of this is that a zinc-iron-sulphate cell is analogous to a copper-lead-sulphate cell, in that it affords a considerably higher effective E.M.F. than corresponds with the net chemical action, viz. from ·398 to ·432 instead of ·284.

Another result is that, since the thermovoltaic constants for cadmium and iron (in solutions 1·0 MSO_4 100 H_2O) are respectively $+\cdot001$ and $+\cdot114$, if iron were to displace cadmium from solution of this strength, there would be evolved $93200-(89880-75)=3395$ gramme-degrees per gramme-molecule (75 being the heat of dilution from $1\cdot0$ $CdSO_4$ $100\,H_2O$ to $\cdot25$ $CdSO_4$ $100\,H_2O$), corresponding with a value for E_H of $\cdot075$ volt, cadmium acquiring the higher potential; but upon this chemical source of potential-difference there is superposed the thermovoltaic action

$$k_1-k_2=+\cdot001-\cdot114=-\cdot113\,;$$

hence the net effective E.M.F. is

$$+\cdot075-\cdot113=-\cdot038:$$

that is, *instead of cadmium acquiring the higher potential, iron does so*, and a current flows with an E.M.F. of $-\cdot038$ volt (mean observed value $=-\cdot035$ volt).

As regards iron-lead-sulphate cells, it is to be remarked that, since lead acquires the higher potential and since the thermovoltaic constant of lead is a considerable negative quantity whilst that of iron is also a considerable positive quantity, the value of k_1-k_2 is largely negative, viz. for solutions of strengths $1\cdot0$ MSO_4 $100\,H_2O$ (zinc-sulphate solution being used to suspend lead sulphate in), $-\cdot200-\cdot114=-\cdot314$. That is to say, whilst the value of E_H corresponding to this displacement of lead from lead sulphate (solid) by iron is $\cdot428$ volt (corresponding with $93200-73800=19400$ gramme-degrees per gramme-molecule), the effective E.M.F. of the cell is little more than one fourth of this, viz. $\cdot428-\cdot314=\cdot114$ (mean observed value $=\cdot112$ volt).

The same kind of remark applies to iron-copper-sulphate cells in a less degree, the value of k_1-k_2 being here (for $1\cdot0$ MSO_4 $100\,H_2O$) $+\cdot009-\cdot114=-\cdot105$; that is, whilst the value of E_H is $\cdot821$ (corresponding with $93200-55960=37240$ gramme-degrees per gramme-molecule), the effective E.M.F. of the cell is only $\cdot821-\cdot105=\cdot716$ (mean observed value $=\cdot715$ volt).

It should consequently result that, if a cell be set up with an electro-silver plate immersed in saturated silver-sulphate solution opposed to bright iron in an equally strong ferrous-sulphate solution, viz. $\cdot042$ $FeSO_4$ $100\,H_2O$, the value of k_1-k_2

will be largely negative, approximating to $-{\cdot}351-{\cdot}148=-{\cdot}499$; so that as E_H is, in this case, 1·605 (corresponding with $93200-20390=72810$ gramme-degrees per gramme-molecule), the effective E.M.F. will be near to $1{\cdot}605-{\cdot}499=1{\cdot}106$ volt. In point of fact, a number of such cells gave on examination the average value 1·103 with a probable error of ±·003 volt.

Effect of varying the Plate-surface in Iron-copper-sulphate Cells; and Rate of Depreciation of E.M.F. of such Cells with increasing Current-density.

176. Some experiments were carried out precisely as described in §§ 115, 124, and 131, with cells set up with polished iron plates immersed in a strong solution of ferrous sulphate opposed to electro-copper plates in copper-sulphate solution. The values obtained show that, whilst with zinc-copper, zinc-cadmium, cadmium-copper, zinc-silver, and copper-silver cells halving the area of the plate on which metal is deposited usually causes a greater decrease in the E.M.F. for a given rate of current-flow than is caused by halving the area of the other plate, the reverse is the case with iron-copper cells. Thus, for example, in one experiment the following numbers were obtained, and similarly in other cases:—

Current in micro-ampères.	Effect of halving area of the	
	Iron plate.	Copper plate.
500	·008	·005
1000	·010	·006
2000	·012	·008
5000	·017	·012
10,000	·027	·021

With iron-copper-sulphate cells the rate at which the E.M.F. of the cell diminishes as the current-density increases is distinctly more rapid than with cadmium-copper-sulphate cells, or with Daniell cells (zinc-copper-sulphate): thus, for instance:—

Rate of current-flow in microampères per square centimetre.	Average E.M.F.	Fall in E.M.F.
0	·711	
20	·708	·003
40	·698	·013
100	·685	·026
200	·671	·040
400	·656	·055
1000	·632	·079
2000	·604	·107

It is noticeable that the substitution of dilute sulphuric acid for ferrous-sulphate solution in an iron-copper cell uniformly tends to *lower* the E.M.F., also rendering the cell-values less permanent and subject to wider ranges of fluctuation than before, probably on account of the "local action" of the acid on the iron; a similar result is also brought about by the substitution of dilute hydrochloric acid for ferrous-chloride solution in cells containing iron and other metals with chloride solutions.

VI. *Magnesium.*

177. Two sets of cells were examined containing bright magnesium (wire) immersed in magnesium-sulphate solution opposed to amalgamated zinc and electro-copper in their sulphate solutions respectively, the solution-strength being 1·0 MSO_4 100 H_2O throughout.

The galvanometer-readings showed a slight increase in each case as time elapsed after first setting up; the following figures represent the mean readings of each cell during the first half hour after setting up, reduced to volts :—

	Magnesium-Zinc.	Magnesium-Copper.
Maximum mean reading ...	·740	1·854
Minimum " " ...	·718	1·827
Average " " ...	·724	1·840
Probable error	±·0042	±·0041

Hence the following valuations of the voltaic constant result; these values are negative, since zinc acquires the higher, and magnesium the lower potential :—

Zinc-Magnesium cell .... $-{\cdot}724$

Magnesium-Copper + Zinc-Copper... $\left\{\begin{matrix}-1{\cdot}840\\+1{\cdot}114\end{matrix}\right\}$ $-{\cdot}726$

Mean $= -{\cdot}725$

Julius Thomsen finds Mg, O, SO_3 aq. $=180180$ for ·25 $MgSO_4$ 100 H_2O, whence for this strength $E_H = -1{\cdot}634$. Moreover, he finds practically no difference between the heats of dilution of magnesium and zinc-sulphate solutions of strength 1·0 MSO_4 100 H_2O, so for this strength also E_H sensibly $= -1{\cdot}634$. Hence the thermovoltaic constant for bright magnesium in 1·0 $MgSO_4$ 100 H_2O is

$$-{\cdot}725 - (-1{\cdot}634) = +{\cdot}909.$$

VII. *Aluminium.*

178. Two sets of cells were examined, containing bright aluminium plates opposed to amalgamated zinc and electro-copper respectively, immersed in sulphate solutions of strength ·5 MSO_4 100 H_2O (instead of using aluminium sulphate, pure potash alum was employed, the potassium sulphate present therein being left out of consideration in valuing the molecular strength). From the heat of formation of aluminium-sulphate solution being greater than that of zinc-sulphate, it might naturally be expected that zinc would acquire the higher potential, as with magnesium-zinc cells ; but this was not the case, aluminium-zinc-sulphate cells resembling cadmium-iron-sulphate cells (§ 175) in that the current actually generated flows in the direction opposite to that predicable from the heats of formation of the electrolytes : for this reason the cell-values are marked with the − sign. The following figures represent the mean readings during the first half hour after setting up: with aluminium-zinc cells the readings slightly diminished in numerical value as time elapsed, and *vice versâ* with the copper-aluminium cells :—

	Zinc-Aluminium.	Aluminium-Copper.
Maximum mean reading ...	−·548	+·588
Minimum " " ...	−·526	+·566
Average " " ..	−·538	+·578
Probable error	±·0034	±·0030

From these figures the following valuations of the voltaic constant result; this constant is of + sign, since aluminium acquires the higher, and zinc the lower potential:—

Zinc-Aluminium .... +·538

$$\text{Zinc-Copper}-\text{Aluminium-Copper}\left\{\begin{array}{c}1{\cdot}114\\-{\cdot}578\end{array}\right\}=+{\cdot}536$$

$$\text{Mean}=+{\cdot}537$$

Julius Thomsen finds that $Al_{\frac{2}{3}}, O, SO_3\,aq.=150630$; whence $E_H=-{\cdot}982$ volt. This value is probably not strictly applicable in the case of the cells now under discussion (which contained potash alum and not aluminium sulphate); but the error introduced by taking this value is but small as compared with the thermovoltaic constant deduced, viz.

$${\cdot}537-(-{\cdot}982)=+1{\cdot}519.$$

VIII. *Mercurous-Zinc-sulphate Cells.*

179. A number of cells were examined consisting of amalgamated-zinc plates immersed in zinc-sulphate solution on the one side, and of pure mercury with a magma of mercurous-sulphate and zinc-sulphate solution on the other, the zinc sulphate being of the same strength on each side: with these cells the E.M.F. continually fell as the solution-strength rose *.

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* It may be noticed that mercurous sulphate is about three times as soluble in saturated zinc-sulphate solution as in distilled water. Three saturated solutions gave, on analysis, numbers represented by the following formulæ:—

Distilled water..................	$\cdot0017\ Hg_2SO_4\ 100\ H_2O$.
Zinc-sulphate solution, about one-third saturated................	$\cdot0042\ Hg_2SO_4,\ 2{\cdot}0\ ZnSO_4,\ 100\ H_2O$.
Saturated zinc-sulphate solution ..	$\cdot0054\ Hg_2SO_4,\ 5{\cdot}75\ ZnSO_4,\ 100\ H_2O$.

It is evident that these cells differ but little from a cold-prepared Clark's cell, the essential difference being that in the latter the zinc rod is not coated with fluid mercury to begin with, and is immersed, not in pure zinc-sulphate solution, but in the same magma of mercurous-sulphate and zinc-sulphate solution as surrounds the mercury. This difference in construction gives rise to a slight difference in E.M.F. with weaker solutions of zinc sulphate, the Clark's cell uniformly reading lowest; with saturated or very strong solutions the difference between the two kinds of cell is less than the experimental errors. Thus the following average values were obtained as the voltaic constants of mercury in contact with mercurous sulphate and $m\,ZnSO_4\,100\,H_2O$, and as the E.M.F.'s of cells like Clark's but set up with $m\,ZnSO_4\,100\,H_2O$ instead of saturated zinc-sulphate solution:—

m.	Voltaic constant.	E.M.F. of Clark's cell.
	Volt.	Volt.
5·75	1·457	1·457
4·89	1·462	1·462
4·33	1·466	1·465
3·58	1·471	1·469
2·7	1·477	1·475
·1	1·514	1·510

The heat of formation of mercurous sulphate being unknown, the corresponding thermovoltaic constants cannot be exactly calculated; in all probability, however, the value of E_H is near to 1·202 volt, the value for mercurous-zinc-nitrate cells, when $m = \cdot 25$ (§ 192), so that the thermovoltaic constant is a large positive quantity, near to $+\cdot 25$ volt at least.

B. *Voltaic and Thermovoltaic Constants of Metals immersed in Solutions of their Chlorides.*

I. *Cadmium.*

180. A number of cells were set up with amalgamated-zinc and electro-cadmium plates, and solutions of equal molecular strength, $m\,MCl_2\,100\,H_2O$, on each side, and examined precisely as before. The following average values were obtained, the probable error in each case being from $\pm\cdot 001$ to $\pm\cdot 002$ volt. The values of E_H annexed are calculated from the

heat-valuations of Julius Thomsen, viz. Zn, Cl_2 aq. = 112840, and Cd, Cl_2 aq. = 96250, for molecular strength ·25 MCl_2 100 H_2O; so that the heat of displacement of cadmium by zinc from chloride solution m $CdCl_2$ 100 H_2O is

$$112840 - h_1 - (96250 - h_2) = 16590 - (h_1 - h_2),$$

where h_1 and h_2 are the heats of dilution of zinc- and cadmium-chloride solutions respectively from the strength m MCl_2 100 H_2O to ·25 MCl_2 100 H_2O: the values of h_1 and h_2 are derived from the table given in § 160, Part VIII.

Value of m.	E.	$16590-(h_1-h_2)$.	E_H.	$E-E_H$.
·25	·330	16590	·366	−·036
·5	·329	16190	·357	−·028
1·0	·324	15340	·338	−·014
2·0	·315	13890	·306	+·009
4·0	·307	12290	·271	+·036
6·0	·296	11390	·251	+·045
8·0	·262	10890	·240	+·022

It is here evident that whilst the voltaic constant for cadmium-zinc-chloride cells continually diminishes as the solution-strength increases, the value of E_H diminishes still more rapidly; so that the thermovoltaic constant is negative for weaker solutions and positive for stronger ones, the actual values of this constant being somewhat larger than those observed with zinc-cadmium-sulphate cells (§ 172), but still always under 5 centivolts. With the sulphate cells the values of the constant were opposite in sign, viz. positive for weaker, and negative for stronger solutions.

II. *Copper.*

181. On immersing a plate of clean metallic copper in a strong solution of cupric chloride, the plate speedily becomes visibly coated with a film of sparingly soluble cuprous chloride formed in virtue of the reaction

$$Cu + CuCl_2 = Cu_2Cl_2.$$

With weaker solution the actual deposition of cuprous chlorides in the solid state is not always noticeable, although its formation and presence are readily detected analytically. It is hence evident that any cell containing as one half a solution of cupric chloride and a copper plate must really contain as the electrolyte on this side a mixture of cuprous chloride with more or less cupric chloride, the film of fluid in immediate contact with the copper plate containing but little if any of the latter salt in solution. In point of fact, on examining a number of similar cells set up with electro-copper plates immersed in ·25 $CuCl_2$ 100 H_2O on the one side and amalgamated-zinc plates immersed in ·25 $ZnCl_2$ 100 H_2O on the other, values were obtained fluctuating between 1·083 and 1·106 volt; whilst another series of analogous values fluctuating between almost exactly the same limits, and averaging practically the same value, was obtained with a corresponding set of cells in which the copper plate was immersed, not in cupric-chloride solution alone to begin with, but in a magma of cuprous-chloride crystals suspended in ·25 $CuCl_2$ 100 H_2O[*]. The values of the two series of observations combined were as follows:—

Maximum E.M.F.	1·106
Minimum „	1·083
Average „	1·0985
Probable error of average value . .	±·0018

It is noticeable in this connection that precisely analogous results were obtained with other sets of cells, containing, on the one hand, cupric chloride alone, and on the other a magma of cuprous-chloride crystals and cupric chloride, when opposed to cadmium; whilst similarly various mercury cells gave substantially the same values whether pure metallic mercury and corrosive-sublimate solution were used, or mercury and a magma of calomel and corrosive-sublimate solution (§ 183).

It results from the above average value that the voltaic constant for electro-copper immersed in ·25 $CuCl_2$ 100 H_2O (or, what is the same thing, a magma of this solution and crystals of cuprous chloride) is +1·0985, when referred to amalgamated zinc immersed in ·25 $ZnCl_2$ 100 H_2O as zero.

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[*] The cuprous chloride was prepared by boiling together copper-sulphate solution with common salt and spongy copper, filtering hot, and allowing cuprous chloride to crystallize out on cooling.

Sensibly the same value results as the sum of the E.M.F.'s of zinc-cadmium and cadmium-copper cells in solutions of strength ·25 MCl_2 100 H_2O throughout. With the latter cells the following numbers were obtained :—

Maximum	·778
Minimum	·756
Average	·769
Probable error	± ·0018

Voltaic constant from Zinc-copper cells . . . . . =1·0985

Do. from Zinc-cadmium + Cadmium-copper cells . . . . . } ·330 + ·769 = 1·099

Mean . . . . =1·099

The heat of displacement of copper from cuprous chloride by zinc with formation of ·25 $ZnCl_2$ 100 H_2O results from Thomsen's values, thus :—

Zn, Cl_2, aq.	112840
Cu_2, Cl_2	65750
	47090 = 1·038 volt.

Whence the thermovoltaic constant for electro-copper in contact with cuprous chloride suspended in cupric-chloride solution of strength ·25 $CuCl_2$ 100 H_2O is 1·099 − 1·038 = + ·061.

The experiments detailed in § 174 indicated that when lead-sulphate was suspended in cadmium-sulphate solution a higher E.M.F. was observed, *cæteris paribus*, with zinc-lead-sulphate cells than when zinc-sulphate solution was employed ; from which it would seem probable that, if cuprous chloride be suspended in zinc-, cadmium-, and copper-chloride solutions in three zinc-copper-chloride cells otherwise alike, the E.M.F. will be smallest in the first case and greatest in the last. This is in fact the case. The following values were obtained in a number of experiments on the point, indicating that the use of cadmium-chloride solution gives values intermediate between those obtained with zinc- and copper-chloride solutions respectively. The solutions were in all cases of strength ·25 MCl_2 100 H_2O.

	Cu_2Cl_2 suspended in zinc chloride.	Cu_2Cl_2 suspended in cadmium chloride.
Maximum E.M.F. ...	·993	1·011
Minimum „ ...	·980	·993
Average „ ...	·988	1·001
Probable error	±·0028	± ·0035

Hence the thermovoltaic constants for electro-copper in contact with cuprous chloride suspended in zinc- or cadmium-chloride solutions of strength ·25 MCl_2 100 H_2O are *negative* in sign, viz.:—

Suspended in zinc-chloride solution . ·988−1·038=−·050
„ cadmium „ „ . 1·001−1·038=−·037

It should hence result that cells set up with electro-cadmium immersed in ·25 $CdCl_2$ 100 H_2O on the one side, and on the other side electro-copper immersed in a magma of cuprous chloride suspended in zinc-chloride solution of the same strength, will have an E.M.F. of ·672−·050−(−·036)=·658; and, similarly, that analogous cells set up with cuprous chloride suspended in cadmium-chloride solution will have an E.M.F. of ·672−·037−(−·036)=·671 (·672 being the E.M.F. corresponding with the heat of displacement of copper from cuprous chloride by cadmium =96250−65750=30500). On setting up a number of such cells the following values were obtained, the averages being sensibly identical with those thus calculated:—

	Cu_2Cl_2 suspended in zinc chloride.	Cu_2Cl_2 suspended in cadmium chloride.
Maximum E.M.F.......	·667	·674
Minimum „	·654	·666
Average „	·659	·671
Probable error	±·0027	±·0016

It is noticeable in connection with these values, that whereas zinc-cadmium, cadmium-copper, and zinc-copper cells set up with sulphate solutions of various strengths possess E.M.F's. in no case differing by more than ±·010 volt from the values calculated from the difference between the heats of formation of the two electrolytes, the divergence between the two values is usually much greater when corresponding cells are set up with chloride solutions. Thus, for example:—

	Calculated.	Observed.	Difference.
Zinc-Cadmium ($\cdot 25\,MCl_2$ $100\,H_2O$) …	·366	·330	− ·036
Do. ($6{\cdot}0\,MCl_2$ $100\,H_2O$) ……	·251	·296	+ ·045
Zinc-Copper (Cu_2Cl_2 in $ZnCl_2$) ………	1·038	·988	− ·050
Do. (Cu_2Cl_2 in $CdCl_2$) ………	1·038	1·001	− ·037
Do. (Cu_2Cl_2 in $CuCl_2$) ………	1·038	1·099	+ ·061
Cadmium-Copper (Cu_2Cl_2 in $ZnCl_2$)…	·672	·659	− ·013
Do. (Cu_2Cl_2 in $CdCl_2$)…	·672	·671	− ·001
Do. (Cu_2Cl_2 in $CuCl_2$)…	·672	·769	+ ·097

III. *Silver.*

182. A number of cells were set up with amalgamated-zinc and zinc-chloride solution on one side, and on the other side electro-silver immersed in a magma of freshly precipitated, well-washed silver chloride, suspended in zinc-chloride solution. The following values were finally obtained for cells where the zinc-chloride solution is of the same strength, $m\mathrm{ZnCl_2}\,100\,\mathrm{H_2O}$, on each side. The probable error is in all cases below ±·003.

The thermovoltaic constants for electro-silver thus immersed are calculated from the heat of displacement of silver from silver chloride by zinc forming $m\mathrm{ZnCl_2}\,100\,\mathrm{H_2O}$, viz.:—

$$112840 - 58760 - h = 54080 - h;$$

where

$$112840 = \mathrm{Zn},\ \mathrm{Cl_2},\ \mathrm{aq.}\ (m = \cdot 25),$$

$$58760 = \mathrm{Ag_2},\ \mathrm{Cl_2},$$

$$h \ = \text{heat of dilution of } m\mathrm{ZnCl_2}\ 100\,\mathrm{H_2O} \text{ to } \cdot 25\,\mathrm{ZnCl_2}\ 100\,\mathrm{H_2O}\ (\S\ 160).$$

m.	k.	$54080-k$.	E_H.	E.	$E-E_H$.
·25	0	54080	1·192	1·080	−·112
·5	400	53680	1·184	1·068	−·116
1·0	1250	52830	1·165	1·049	−·116
3·0	3800	50280	1·109	1·026	−·083
6·0	5300	48780	1·076	1·014	−·062

Hence it results that both the voltaic and thermovoltaic constants diminish in value as the solutions become stronger; and that whilst the thermovoltaic value of silver in contact with silver chloride (suspended in zinc-chloride solution) is negative in sign as with the sulphate, its numerical value is considerably less than in that instance.

Some cells were next examined, containing on the one side electro-silver plates immersed in a magma of silver chloride suspended in zinc-chloride solution, and on the other side electro-copper or electro-cadmium in their respective chloride solutions, the solution-strength being $\cdot 25 MCl_2 100 H_2O$ throughout. The following values were obtained, sensibly agreeing with the value −·112 for the thermovoltaic constant above obtained with zinc-silver-chloride cells for this molecular strength. It is to be noticed that the values of E_H with these two kinds of cells respectively are ·827 and ·154, corresponding with the heat-evolutions $96250-58760=37490$, and $65750-58760=6990$. In the former case $E_H+(k_1-k_2)$ is positive in sign, in the latter case negative; so that the copper-silver cells are analogous to the zinc-cadmium-sulphate and cadmium-iron-sulphate cells above described, in that the metal actually acquiring the higher potential is not the one predicable from the formation-heats of the electrolytes, but the other one—a result indicated by the − sign prefixed to the values of E.

	Cadmium-Silver.	Copper-Silver.
Maximum E.M.F. observed......	·758	−·017
Minimum ,, ,, ...	·743	−·025
Average ,, ,, ...	·751	−·020
Probable error	±·0017	±·0015
Value of thermovoltaic constant deduced from average observed E.M.F.	+ .751 + ·330 +1·081 −1·192 −·111	− ·020 +1·099 +1·079 −1·192 −·113

The general average of the three values −·112, −·111, and −·113 thus obtained with zinc-silver, cadmium-silver, and copper-silver cells respectively is −·112, representing the thermovoltaic constant for electro-silver in contact with precipitated silver chloride suspended in zinc-chloride solution of strength ·25 $ZnCl_2$ 100 H_2O.

In precisely similar fashion six other kinds of cells were examined, containing respectively zinc in zinc-chloride, cadmium in cadmium-chloride, and copper in cupric-chloride solutions, opposed in one series to silver immersed in silver chloride suspended in cadmium-chloride solution, and in the other to silver immersed in silver chloride suspended in cupric-chloride solution, the solution-strength being ·25 MCl_2 100 H_2O throughout. In the copper-silver cells, where the silver chloride was suspended in cadmium-chloride solution, the same peculiarity is observable as when suspended in zinc-chloride solution, viz. that the copper, and not the silver, acquires the higher potential; but where the silver chloride is suspended in cupric-chloride solution this is not the case, the silver here acquiring the higher potential, and the current flowing in the direction predicable from the heats of formation of the electrolytes, and not in the opposite direction. The following values were obtained :—

Silver Chloride suspended in Cadmium-Chloride Solution.

	Zinc-Silver.	Cadmium-Silver.	Copper-Silver.
Maximum	1·091	·766	−·009
Minimum	1·082	·757	−·014
Average	1·088	·761	−·010
Probable error	± ·0010	±·0010	±·0012

Silver Chloride suspended in Cupric-Chloride Solution.

Maximum	1·139	·809	+·038
Minimum	1·128	·806	+·031
Average	1·136	·807	+·035
Probable error	± ·0017	±·0006	±·0015

From these figures the following concordant values result for the thermovoltaic constants of electro-silver immersed in silver chloride suspended in cadmium and copper chlorides respectively :—

Silver Chloride suspended in Cadmium-Chloride Solution.

		E.	E_H.	$E-E_H$.
Zinc-Silver cells		1·088	1·192	−·104
Cadmium-Silver + Zinc-Cadmium	+ ·761 + ·330	1·091	1·192	−·101
Copper-Silver + Zinc-Copper ...	+1·099 − ·010	1·089	1·192	−·103
	Average	1·089		−·103

Silver Chloride suspended in Cupric-Chloride Solution.

Zinc-Silver cells		1·139	1·192	−·053
Cadmium-Silver + Zinc-Cadmium	+ ·807 + ·330	1·137	1·192	−·055
Copper-Silver + Zinc-Copper......	+1·099 + ·035	1·134	1·192	−·058
	Average	1·137		−·055

It is noticeable that suspending silver chloride in zinc-, cadmium-, or copper-chloride solution affects the E.M.F. of a cell in the same way as the use of the same fluids for the suspension of cuprous chloride (§ 181), viz. that the E.M.F. is lowest with zinc and highest with copper-chloride solution.

Since the E.M.F. of a zinc-silver-chloride cell continually diminishes as the solution-strength rises, just as with a Clark's cell (§ 179), it is evident that De-la-Rue and Müller's cell must possess an E.M.F. variable with the strength and nature of the solution used. A number of rods of pure silver chloride fused round strips of pure silver were obtained from Messrs. Johnson and Matthey, and set up opposed to zinc and cadmium in various solutions of their chlorides respectively. Variations of 4 to 5 centivolts were observed in the E.M.F.'s of such cells with different silver-chloride rods, everything else being the same, and the observations being made with the electrometer to avoid possible diminution in E.M.F. The average values found were slightly lower than those found with the same solution-strengths and precipitated silver chloride, as might perhaps be expected, inasmuch as the silver strips inside the fused rods were not electro-coated but were of bright metal, which has been found in the case of sulphate-cells to give lower values than electro-coated metal (§ 125).

	Zinc-Silver.		Cadmium-Silver.	
	·25 $ZnCl_2$ 100 H_2O.	2·0 $ZnCl_2$ 100 H_2O.	·25 $CdCl_2$ 100 H_2O.	2·0 $CdCl_2$ 100 H_2O.
Maximum	1·097	1·048	·776	·740
Minimum	1·058	·995	·726	·714
Average	1·075	1·020	·750	·730
Value with precipitated silver chloride	1·080	1·037	·761	...

IV. *Mercury.*

183. When metallic mercury and corrosive-sublimate solution are brought into contact, calomel is formed; so that by agitating the two together almost the whole of the metal and chlorine are removed from solution. Hence it is to be expected that the same peculiarity would apply to these cells

as to copper cells (§ 181), viz. that much the same E.M.F. will be given whether mercury be in contact with corrosive-sublimate solution, or with a magma of calomel and corrosive-sublimate solution. In point of fact this is the case; cells set up in the two ways with the mercury opposed to cadmium (or zinc) giving values as nearly identical as the considerably wide range of fluctuation in E.M.F. observed with different cells would permit to be deduced. In each case the values ranged between ·89 and ·95 volt (cadmium), and between 1·21 and 1·28 (zinc). Combining the two sets of cells, the following values were obtained, the solution being ·25 MCl_2 100 H_2O throughout.

	Zinc-Mercury.	Cadmium-Mercury.
Maximum	1·282	·948
Minimum	1·207	·892
Average	1·256	·929
Probable error ...	± ·0056	± ·0053

From these two values nearly the same voltaic constant is deduced for mercury in contact with mercuric-chloride solution (or with a magma of mercuric chloride suspended in mercuric-chloride solution) of strength ·25 $HgCl_2$ 100 H_2O.

Zinc-mercury . . . . 1·256

Cadmium-mercury + Zinc-cadmium . $\left\{\begin{matrix}\cdot 929\\ \cdot 330\end{matrix}\right\} = 1{\cdot}259$

Mean . . . . $\overline{1{\cdot}257}$

Since $Hg_2, Cl_2 = 82550$, the value of E_H corresponds with 112840 − 82550 = 30290 gramme-degrees for zinc-mercury-chloride cells, and with 96250 − 82550 = 13700 for cadmium-mercury-chloride cells, or ·668 and ·302 volt respectively; whence evidently both classes of cells resemble lead-copper-sulphate cells (§ 174) in actually giving rise to an E.M.F. greatly superior to that corresponding with the net chemical change. The thermovoltaic constant deduced from the above mean voltaic constant is 1·257 − ·668 = + ·589; so that mercury in this class of cells resembles iron, aluminium, and magnesium in their sulphate cells, possessing a large positive thermovoltaic constant.

Some observations were next made with cells containing calomel suspended in zinc-chloride solution in contact with mercury on one side, and amalgamated zinc immersed in the same zinc-chloride solution on the other side. Like the analogous zinc-silver-chloride, zinc-lead-sulphate, and zinc-mercury-sulphate cells above described, the E.M.F. of this combination was found to decrease as the solution-strength rises. Thus the following numbers were obtained with solution-strengths $m\mathrm{ZnCl_2}\ 100\,\mathrm{H_2O}$, the probable error being from ±·002 to ±·003 in each case.

$m=\cdot 25$	1·123
$=1\cdot 0$	1·093
$=5\cdot 0$	1·043
$=9\cdot 5$	·988

From these values the following thermovoltaic constants result, the values of E_H being calculated from the heat-values $112840-82550-h=30290-h$, where h is heat of dilution of $m\mathrm{ZnCl_2}\ 100\,\mathrm{H_2O}$ to $\cdot 25\,\mathrm{ZnCl_2}\ 100\,\mathrm{H_2O}$.

m.	h.	$30290-h$.	E_H.	E.	$E-E_H$.
·25	0	30290	·668	1·123	+·455
1·0	1250	29040	·640	1·093	+·453
5·0	4800	25490	·562	1·043	+·481
9·5	6000	24290	·536	·988	+·452

Observations with cells containing electro-cadmium immersed in $\cdot 25\mathrm{CdCl_2}\ 100\,\mathrm{H_2O}$ opposed to mercury in contact with calomel suspended in zinc-chloride solution of the same strength led to nearly the same value for the thermovoltaic constant when $m=\cdot 25$:—

Maximum E.M.F. observed . . .	·806
Minimum " " . .	·791
Average " " . .	·799
Probable error	±·0030

		Voltaic constant.	$E-E_H$.
Zinc-cadmium + Cadmium-mercury...	$\left\{\begin{matrix}\cdot 799\\ \cdot 330\end{matrix}\right\}$	= 1·129	+·461
Zinc-mercury cells........		= 1·123	+·455
Mean		1·126	+·458

Substituting cadmium-chloride solution for zinc-chloride solution as the menstruum in which the calomel is suspended raises the value of E, as might be anticipated from various analogous results above described. Thus the following values were obtained with zinc-mercurous-chloride and cadmium-mercurous-chloride cells so set up, the amalgamated-zinc plates being surrounded by zinc-chloride, and the electro-cadmium plates employed with cadmium-chloride solution, the solution-strength being uniformly $\cdot 25\,MCl_2\ 100\,H_2O$.

	Zinc-Mercury.	Cadmium-Mercury.
Maximum E.M.F. observed......	1·144	·815
Minimum " "	1·137	·808
Average " "	1·140	·812
Probable error	± ·0013	± ·0014

From these figures the following values result as the thermo-voltaic constant for mercury in contact with calomel suspended in $\cdot 25\,CdCl_2\ 100\,H_2O$:—

	E.	E_H.	$E-E_H$.
Zinc-mercury	1·140	·668	+·472
Cadmium-mercury . $\left\{\begin{matrix}\cdot 812\\ \cdot 330\end{matrix}\right\}$	1·142	·668	+·474
Mean . .	1·141		+·473

From the values of the heats of formation of silver chloride and mercurous chloride respectively, it might, *à priori*, be expected that an E.M.F. of +·525 should result (corresponding with 82550−58760=23790 gramme-degrees) in silver-mercury-chloride cells, silver acquiring the higher potential. On the other hand, whether the silver chloride be suspended in zinc or cadmium-chloride solutions, and whether the mercurous chloride be similarly suspended, in all four cases the value of k_1-k_2 is not only negative, but is numerically greater than $E_H=\cdot 525$; so that, in fine, the current flows in the opposite direction to that *à priori* predicable, the mercury acquiring the higher potential. Then the E.M.F.'s of the four kinds of silver-mercury-chloride cells are as follows:—

Calculated from formula $E=E_H+k_1-k_2$.			Observed.		
AgCl suspended	Hg_2Cl_2 suspended		Maximum.	Minimum.	Average.
in $ZnCl_2$ ...	in $ZnCl_2$ ...	·525+(−·112)−·458=−·045	−·040	−·051	−·046
Ditto ...	in $CdCl_2$ ...	·525+(−·112)−·473=−·060	−·055	−·062	−·058
in $CdCl_2$ ...	in $ZnCl_2$ ...	·525+(−·103)−·458=−·036	−·034	−·041	−·038
Ditto ...	in $CdCl_2$ ...	·525+(−·103)−·473=−·051	−·047	−·053	−·050

Considerably larger negative values were obtained with analogous cells in which mercurous chloride was suspended in mercuric-chloride solution instead of zinc or cadmium-chloride solution, as would naturally be inferred from the larger values of the thermovoltaic constant in this case. The observed values ranged between −·134 and −·187, averaging −·167, that deduced as the above being −·176.

V. *Lead.*

184. A number of cells were examined, set up with electro-lead plates immersed in saturated lead-chloride solution, opposed (*a*) to amalgamated zinc in zinc-chloride solution; (*b*) to electro-cadmium in cadmium-chloride solution; (*c*) to electro-silver immersed in silver chloride suspended in zinc-chloride solution; the solution-strength being $·05\,MCl_2$ $100\,H_2O$ throughout. The following values were obtained:—

	Zinc-Lead.	Cadmium-Lead.	Lead-Silver.
Maximum	·596	·268	·504
Minimum	·586	·248	·484
Average	·591	·260	·489
Probable error ...	±·0017	±·0023	±·0024

These numbers give the following valuations for the voltaic constant of electro-lead in the lead-chloride solution:—

Zinc-lead . . . . = ·591
*Zinc-cadmium + Cadmium-lead . ·260 + ·330 = ·590
*Zinc-silver − Silver-lead . . . 1·080 − ·489 = ·591
Mean . . = ·591

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* The zinc-cadmium and zinc-silver values are assumed to be the same for the solution-strength used as those above found for somewhat stronger solutions $·25\,MCl_2$ $100\,H_2O$; the error thus introduced is but small, if not inappreciable.

Since Pb, Cl_2 aq. = 75970, the value of E_H is ·813 (corresponding with 112840 − 75970 = 36870 gramme-degrees); whence the thermovoltaic constant for electro-lead in saturated lead-chloride solution is ·591 − ·813 = − ·222.

It is noteworthy that whilst $k_1 - k_2$ is negative for both zinc-lead and cadmium-lead cells, so that their electromotive forces are notably below the values corresponding with the heat-evolution during the net chemical change, the reverse is the case for lead-silver cells: here the heat-evolution is 75970 − 58760 = 17210 gramme-degrees, corresponding with ·379 volt; whilst the actual E.M.F. is ·379 + (− ·112) − (− ·222) = ·489 volt (observed average = ·489 volt). So that whilst lead-silver-sulphate cells give rise to electromotive forces considerably *below* the value of E_H pertaining to that class of cell, lead-silver-chloride cells possess electromotive forces considerably *above* the corresponding value of E_H.

On substituting lead-chloride solution for zinc-chloride solution as the medium in which silver chloride is suspended, but little change is produced in the E.M.F. Thus a number of lead-silver-chloride cells containing solution of strength $·25 PbCl_2\ 100 H_2O$ throughout gave values ranging from ·453 to ·522 volt, and averaging near to ·480.

Some lead-copper-chloride cells were examined; but for some unknown reason they failed to give concordant results, the observed E.M.F. always falling short of that deduced from the voltaic constants for lead and copper in chloride-solution (viz. 1·099 − ·591 = ·508). In some cases the falling off was small; in others it exceeded ·050: these cells, moreover, exhibited no constancy even for half an hour after setting up, the E.M.F. rapidly falling as time elapsed. In all cases, however, higher electromotive forces were observed than correspond with the difference between Pb, Cl_2 aq. = 75970 and Cu_2, Cl_2 = 65750, viz. 10220 gramme-degree = ·225 volt.

On the other hand, numbers closely agreeing with those calculated from the above-described thermovoltaic constants were obtained with cells set up with electro-lead immersed in lead-chloride opposed to mercury in contact with mercurous chloride suspended in zinc- or cadmium-chloride solution, the strength being $·25 MCl_2\ 100 H_2O$ throughout. The value of E_H in these cells is + ·145 volt, corresponding with

82550−75970=6580 gramme-degrees, the metal giving the smaller heat-value, and consequently acquiring the higher potential in consequence of the chemical action, being lead. Since, however, the thermovoltaic constant for lead is −·222, and that for mercury in contact with mercurous chloride suspended in zinc-chloride solution +·458, and when suspended in cadmium-chloride solution +·473, the value of $k_1 - k_2$ is in each case largely negative, and considerably greater numerically than E_H. Hence the calculated electromotive forces for the two cells are respectively ·145+(−·222)−·458 =−·535, and ·145+(−·222)−·473=−·550 volt. The observed values were −·539 and −·549 respectively, *i. e.* electromotive forces of ·539 and ·550 volt were observed, the mercury, and not the lead, acquiring the higher potential. These cells are remarkable not only for the large negative values of $k_1 - k_2$, but also for the high negative values of $E_H + k_1 - k_2$, exceeding in this respect all other cells examined with the exception of zinc-aluminium-sulphate cells (§ 178), which gave the numerical value ·537.

VI. *Magnesium.*

185. A series of cells was set up containing bright magnesium (wire) opposed to amalgamated zinc and electro-cadmium in their respective chloride-solutions, the strength being uniformly $\cdot 25\,MCl_2\ 100\,H_2O$. The values exhibited much greater fluctuations as time elapsed than were observed with most of the other cells examined; whilst the mean readings during the first half-hour after setting up also showed much less concordance, as the following figures show. As with the sulphate-cells (§ 177), magnesium acquired the lower potential when opposed to zinc, and *à fortiori* when opposed to cadmium.

	Magnesium-Zinc.	Magnesium-Cadmium.
Maximum	·771	1·101
Minimum	·636	·966
Average	·702	1·030
Probable error ...	±·012	± ·012

Hence the following valuations of the voltaic constant result, these values necessarily being negative, as with the sulphate-cells:—

$$\begin{array}{lr} \text{Zinc-magnesium cell} \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. & -\cdot 702 \\ \text{Cadmium-magnesium} - \text{Zinc-cadmium} \left\{\begin{matrix} -1\cdot 030 \\ +\ \cdot 330 \end{matrix}\right\} & -\cdot 700 \\ \hline \text{Mean} \;.\;.\;. & -\cdot 701 \end{array}$$

Julius Thomsen finds $Mg, Cl_2 aq. = 186930$ for solution of strength $\cdot 25\, MgCl_2\, 100\, H_2O$; whence $E_H = -1\cdot 634$. Consequently the thermovoltaic constant for bright magnesium in contact with chloride solution of this strength is

$$-\cdot 701 - (-1\cdot 634) = +\cdot 933,$$

or, approximately, the same large positive quantity as that found with sulphate solutions.

VII. *Aluminium.*

186. In precisely the same way were two series of observations made with cells containing plates of bright aluminium opposed to amalgamated zinc and electro-cadmium immersed in solutions of their chlorides respectively, the solution-strength being $\cdot 25\, Al_{\frac{2}{3}}\, Cl_2\, 100\, H_2O$*, and equivalent amounts throughout. As with the magnesium cells, the values fluctuated considerably, so that the final averages had much larger probable errors than usual.

	Zinc-Aluminium.	Aluminium-Cadmium.
Maximum	$-\cdot 239$	$+\cdot 091$
Minimum	$-\cdot 352$	$-\cdot 022$
Average	$-\cdot 280$	$+\cdot 050$
Probable error	$\pm\cdot 011$	$\pm\cdot 011$

Each of these averages leads to the same value, $+\cdot 280$, for this voltaic constant.

$$\begin{array}{lr} \text{Zinc-aluminium} \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. & +\cdot 280 \\ \text{Zinc-cadmium} - \text{Aluminium-cadmium} \left\{\begin{matrix} +\cdot 330 \\ -\cdot 050 \end{matrix}\right\} & +\cdot 280 \\ \hline \text{Mean} \;.\;.\;. & +\cdot 280 \end{array}$$

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* The aluminium-chloride solution was prepared by saturating dilute hydrochloric acid with recently precipitated well-washed aluminium hydroxide.

This constant being of + sign, since aluminium was found to acquire the higher and zinc the lower potential (as with the sulphate-cells, § 178); whilst, on the other hand, the readings observed with the zinc-aluminium cells are marked − above, because this cell is another example of the case where $E_H+k_1-k_2$ has a negative value, the current actually set up passing in the direction opposite to that predicable from the heats of formation of the electrolytes.

Julius Thomsen finds $Al_{\frac{2}{3}}, Cl_2$ aq. = 158550, whence $E_H = -1{\cdot}008$; consequently

$$E-E_H=+{\cdot}280-(-1{\cdot}008)=+1{\cdot}288;$$

i. e. the thermovoltaic constant for bright aluminium in contact with its chloride solution is a large positive quantity, as with the sulphate.

VIII. *Iron.*

187. Cells were set up containing plates of nearly pure sheet-iron (bright) opposed to amalgamated zinc and electro-cadmium in solution of constant strength $\cdot 25\,MCl_2\ 100H_2O$; also to electro-silver immersed in a magma of precipitated silver-chloride suspended in zinc-chloride solution of this same strength. The following numbers were obtained as the average readings during the first half-hour after setting up.

	Zinc-Iron.	Cadmium-Iron.	Silver-Iron.
Maximum	·497	−·154	·597
Minimum	·483	−·167	·583
Average	·490	−·157	·592
Probable error ...	±·0030	±·0027	±·0033

Hence the following three valuations for the voltaic constant result; the values with the cadmium-iron cell being marked −, since in this case (as with the corresponding sulphate cells, § 175) iron, and not cadmium, actually acquires the higher potential.

$$\begin{array}{lr} \text{Zinc-iron} \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. & \cdot 490 \\ \text{Zinc-cadmium}-\text{Cadmium-iron} \;. \left\{\begin{array}{r} \cdot 330 \\ +\cdot 157 \end{array}\right\} = & \cdot 487 \\ \text{Zinc-silver}-\text{Iron-silver} \;.\;.\;. \left\{\begin{array}{r} 1\cdot 080 \\ -\cdot 592 \end{array}\right\} = & \cdot 488 \\ \text{Mean} \;.\;.\;. & \cdot 488 \end{array}$$

Julius Thomsen finds Fe, Cl_2 aq. = 99950 for ·25$FeCl_2$, 100H_2O; whence $E_H = \cdot 284$. Hence the thermovoltaic constant for bright metallic iron in ferrous-chloride solution of this strength is

$$E - E_H = \cdot 488 - \cdot 284 = + \cdot 204 ;$$

i. e. it is a considerable *positive* quantity, as in the case of the sulphate-cells.

It is noticeable that whilst with silver-iron cells the value of $k_1 - k_2$ is negative, so that E is considerably less than E_H, the opposite holds with zinc-iron cells, the E.M.F. actually set up being not much below double that corresponding with the net heat-development in the cell.

C. *Voltaic and Thermovoltaic Constants of Metals immersed in Solutions of their Nitrates.*

I. *Copper.*

188. A number of cells were set up with amalgamated-zinc and electro-copper plates, and solutions of the nitrates of the respective metals prepared by dissolving pure metals in nitric acid, and saturating any excess of acid by means of the metallic carbonate freshly precipitated from a portion of the respective solution, and well washed. The following values were obtained as the mean readings during the first twenty minutes after setting up. The readings during this period did not always exhibit constancy, especially with the weaker solutions; but the extreme alteration usually only amounted to a few millivolts, concurrently with a visible alteration in the surfaces of the plates. Strength of solutions, $m M(NO_3)_2$ 100H_2O.

	$m = \cdot 25$.	$m = 1\cdot 0$.	$m = 2\cdot 0$.	$m = 8\cdot 0$.
Maximum	1·087	1·104	1·112	1·095
Minimum	1·053	1·073	1·108	1·087
Average............	1·066	1·089	1·109	1·091
Probable error ...	±·0035	±·0034	±·0005	±·0009

These figures correspond with the following thermovoltaic constants, the values of E_H being deduced from the experiments of Julius Thomsen, including his valuations of the heats of dilution of zinc- and copper-nitrate solutions. The difference between the heats of formation of $m\mathrm{M(NO_3)_2}$ $100\mathrm{H_2O}$ are given by the formula

$$102510-h_1-(52410-h_2)=50100-(h_1-h_2),$$

where Zn, O, $\mathrm{N_2O_5}$ aq. = 102510, and Cu, O, $\mathrm{N_2O_5}$ aq. = 52410 for solution-strengths $\cdot25\ \mathrm{M(NO_3)_2}, 100\ \mathrm{H_2O}$; whilst h_1 and h_2 are the heats of dilution of solutions of zinc and copper nitrate respectively from the strength $m\mathrm{M(NO_3)_2}\ 100\ \mathrm{H_2O}$ to $\cdot25\ \mathrm{M(NO_3)_2}\ 100\ \mathrm{H_2O}$.

m.	h_1.	h_2.	$50100-(h_1-h_2)$.	$\mathrm{E_H}$.	E.	$\mathrm{E}-\mathrm{E_H}$.
·25	0	0	50100	1·105	1·066	−·039
1·0	− 40	− 47	50093	1·105	1·089	−·016
2·0	−132	−175	50057	1·104	1·109	+·005
8·0	+439	+214	49875	1·100	1·091	−·009

It is here noticeable that the thermovoltaic constant for electro-copper in nitrate solution has in no case any large value; whilst of negative sign for low-solution strengths, it becomes positive for stronger fluids, and again negative with highly concentrated solutions, following the variations in the voltaic constant, which has a maximum value for fluids of medium strength.

II. *Cadmium.*

189. Cells were set up with electro-cadmium plates immersed in cadmium-nitrate solution, opposed on the one hand to electro-copper, and on the other to amalgamated zinc immersed in solutions of their nitrates respectively, the constant solution-strength being $\cdot25\ \mathrm{M(NO_3)_2}\ 100\ \mathrm{H_2O}$. The following values were obtained:—

	Zinc-Cadmium.	Cadmium-Copper.
Maximum	·359	.722
Minimum	·344	·707
Average	·351	·713
Probable error ...	±·0026	±·0024

From these figures the following valuations result for the voltaic constant of cadmium in nitrate solution $\cdot 25\,\mathrm{Cd(NO_3)_2}\ 100\,\mathrm{H_2O}$:—

Zinc-cadmium		·351
Zinc-copper − Cadmium-copper	1·066 − ·713	= ·353
	Mean	= ·352

Julius Thomsen finds Cd, O, $\mathrm{N_2O_5}$ aq. = 86300 (for $\cdot 25\,\mathrm{Cd(NO_3)_2}\,100\mathrm{H_2O}$), whence $E_H = \cdot 357$. Hence the thermovoltaic constant for electro-cadmium in nitrate solution of this strength is

$$E - E_H = \cdot 352 - \cdot 357 = -\cdot 005.$$

It is here noticeable that the value of the thermovoltaic constant is negative, as in the case of chloride solution of corresponding strength, whereas it is positive in the case of sulphate solution of the same strength; but in no case is the numerical value of the constant large.

III. *Lead.*

190. Cells containing electro-lead opposed to amalgamated zinc and electro-copper in nitrate solution of strength $m\mathrm{M\,(NO_3)_2}\ 100\,\mathrm{H_2O}$ gave the following average values, the probable error in no case exceeding ±·004, and being usually considerably less:—

	$m = \cdot 25$.	$m = 1\cdot 0$.	$m = 2\cdot 0$.
Zinc-Lead	·580	·588	·591
Lead-Copper	·486	·501	·519

These two sets of figures lead to practically identical valuations of the voltaic constant:—

	$m = \cdot 25$.	$m = 1\cdot 0$.	$m = 2\cdot 0$.
Zinc-Lead	·580	·588	·591
Zinc-Copper − Copper-Lead	$\left\{\begin{matrix} 1\cdot 066 \\ \cdot 486 \end{matrix}\right\}$ ·580	$\left\{\begin{matrix} 1\cdot 089 \\ \cdot 501 \end{matrix}\right\}$ ·588	$\left\{\begin{matrix} 1\cdot 109 \\ \cdot 590 \end{matrix}\right\}$ ·590
Mean	·580	·588	·591

Taking the valuations of Julius Thomsen, including his determinations of the heats of dilution of zinc- and lead-nitrate solution, h_1 and h_2 respectively, the following values result for E_H, the value of Pb, O, N_2O_5 aq. being 68070 for $\cdot 25\ Pb(NO_3)_2\ 100\ H_2O$:—

m.	h_1.	h_2.	H.	E_H.	E.	$E-E_H$.
·25	0	0	34449	·759	·580	−·179
1·0	− 40	−1274	33206	·732	·588	−·144
2·0	−132	−2092	32462	·716	·591	−·125

Hence the thermovoltaic constant for electro-lead in nitrate solution is always negative (as with sulphate and chloride); the numerical value, however, decreases with increasing solution-strength, whilst the opposite is the case with lead sulphate, whether suspended in zinc- or in cadmium-sulphate solution.

Lead-copper-nitrate cells resemble lead-copper-sulphate cells in that they give an E.M.F. notably above that calculable from the net heat-evolution taking place in the cell due to the chemical change. Similarly zinc-lead-nitrate cells resemble zinc-lead-sulphate cells in giving values below those thus calculable.

IV. *Silver.*

191. The following mean values were obtained with cells set up with electro-silver plates opposed to amalgamated zinc, electro-copper, and electro-lead in nitrate solutions of strength $mM(NO_3)_2$, 100 H_2O (the probable error ranged from ± ·002 to ± ·004 throughout):—

m.	Zinc-Silver.	Copper-Silver.	Lead-Silver.
·25	1·495	·429	·914
1·0	1·540	·450	·951
2·0	1·556	·446	·965

From these figures sensibly identical values result for the voltaic constant of electro-silver in nitrate solution:—

	$m=\cdot25$.		$m=1\cdot0$.		$m=2\cdot0$.	
Zinc-Silver		1·495		1·540		1·556
Zinc-Copper + Copper-Silver	1·066 ·429	1·495	1·089 ·450	1·539	1·109 ·446	1·555
Zinc-Lead + Lead-Silver	·580 ·914	1·494	·588 ·951	1·539	·591 ·965	1·556
Mean ...		1·495		1·539		1·556

The heats of dilution of silver-nitrate solutions being as yet undetermined, the value of E_H can only be exactly calculated for the strength $\cdot25\,Ag_2(NO_3)_2\,100\,H_2O$. The subjoined values for the higher strengths are calculated on the supposition that the heat of dilution of silver- and zinc-nitrate solutions is the same; so that E_H remains the same for all solution-strengths Ag_2, O, N_2O_5 aq.$=16780$.

m.	E.	E_H.	$E-E_H$.
·25	1·495	1·890	−·395
1·0	1·539	1·890	−·351
2·0	1·556	1·890	−·334

Hence the thermovoltaic constant for silver in nitrate solution is not widely different from that in sulphate solution, being in each case far greater than that for silver in contact with silver chloride, whether suspended in zinc cadmium or cupric-chloride solution. With all three kinds of silver salt, however, under all circumstances, the value is negative in sign.

V. *Mercury.*

192. Mercuric-nitrate solution, like mercuric chloride, becomes rapidly and completely converted into mercurous salt by agitation with mercury. In order to prepare mercurous nitrate with but little excess of acid, mercury was dissolved in nitric acid, and the crystallized mass washed on the filter-pump with a little water, and then well agitated with water and mercury. The solution thus obtained was free from

mercuric nitrate, and contained free nitric acid to an amount representing almost exactly one eighth of that present as mercurous nitrate, and was finally made of strength ·25 $Hg_2(NO_3)_2$, ·03 $H_2(NO_3)_2$ 100 H_2O. On setting up cells with pure mercury and this fluid, opposed to amalgamated zinc, electro-copper, electro-lead, and electro-silver respectively in contact with solutions of their nitrates of constant strength ·25 $M(NO_3)_2$ 100 H_2O, the following values were obtained. It is noticeable that with the last cell the current sometimes passed from mercury to silver and sometimes in the opposite direction, the average E.M.F. being negative,—*i. e.* mercury, and not silver, acquiring the higher potential, contrary to the result predicable from the relative heats of formation of mercurous and silver nitrates (viz. 47990 and 16780 respectively —Julius Thomsen), which corresponds with an E.M.F. of ·688 volt, silver acquiring the higher potential. The probable error amounted to ±·003 to ±·004 in each instance.

	Maximum.	Minimum.	Average.
Zinc-Mercury	1·535	1·476	1·500
Copper-Mercury	·470	·410	·433
Lead-Mercury	·944	·896	·917
Silver-Mercury	−·041	+·019	−·004

Practically identical values for the voltaic constant for mercury in contact with mercurous-nitrate solution result in all four cases:—

$$\text{Zinc-mercury} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad 1·500$$

$$\text{Zinc-copper} + \text{Copper-mercury} \; . \left\{\begin{matrix} 1·066 \\ ·433 \end{matrix}\right\} = 1·499$$

$$\text{Zinc-lead} + \text{Lead-mercury} \; . \; . \left\{\begin{matrix} ·917 \\ ·580 \end{matrix}\right\} = 1·497$$

$$\text{Zinc-silver} - \text{Mercury-silver} \; . \left\{\begin{matrix} 1·495 \\ + ·004 \end{matrix}\right\} = 1·499$$

$$\text{Mean} \; . \; . \; . \; . = \overline{1·499}$$

The average value is thus but slightly below that found for mercury in contact with mercurous sulphate suspended in weak zinc sulphate, viz. 1·514 (§ 179).

Since E_H represents a distinctly less amount (1·202 volt), it results that $E-E_H=1·499-1·202=+·297$; *i.e.* the thermovoltaic constant for mercury in contact with mercurous-nitrate solutions is a considerable + number, as found in the chloride-cells.

It hence follows that the E.M.F. actually set up in zinc-mercury, copper-mercury, and lead-mercury nitrate-cells is in excess of that corresponding with the difference between the heats of formation of the electrolytes in each case respectively, the excess amounts being +·297, +·297−(−·039)=+·336, and +·298−(−·179)=+·477 respectively.

VI. *Magnesium.*

193. Two sets of cells were examined containing bright magnesium (wire), opposed to amalgamated zinc and electro-cadmium respectively, in solutions of constant strength $·25\ M(NO_3)_2\ 100\ H_2O$. The following values were obtained, the readings exhibiting the same kinds of fluctuations as those previously found with magnesium sulphate and chloride cells.

	Magnesium-Zinc.	Magnesium-Copper.
Maximum	·570	1·636
Minimum	·503	1·569
Average	·531	1·595
Probable error	±·011	±·011

These two sets of readings lead to sensibly the same values for the voltaic constant, which is negative (as with the sulphate and chloride cells), since zinc now acquires the higher potential.

Zinc-magnesium . . . . −·531

Copper-magnesium . . . $\begin{Bmatrix}-1·595\\+1·066\end{Bmatrix}$ −·529

Mean . . . . . −·530

From Julius Thomsen's figures, the heat of formation of magnesium-nitrate solution, $·25\ Mg(NO_3)_2\ 100\ H_2O$, is 176480, whence $E_H=-1·631$. Hence the thermovoltaic constant is

$$-·530-(-1·630)=+1·101,$$

or positive to a great extent, as with the other magnesium-cells.

D. *Voltaic and Thermovoltaic Constants of Metals immersed in Solutions of their Acetates.*

I. *Copper.*

194. A number of cells were set up with amalgamated-zinc and electro-copper plates immersed in solutions of their respective acetates, the constant molecular strength being $\cdot 25\ M(C_2H_3O_2)_2H_2O$ *. The following values were obtained:—

Maximum	1·104
Minimum	1·073
Average	1·091
Probable error . . .	·0029

Julius Thomsen's thermochemical data lead to the values $Zn, O, 2C_2H_4O_2aq. = 100710$, and $Cu, O, 2\ C_2H_4O_2aq. = 50340$; whence $E_H = 1\cdot 111$, corresponding with 50370 gramme-degrees. Hence $E - E_H = -\cdot 020$ for electro-copper in contact with copper-acetate solution of strength $\cdot 25\ Cu(C_2H_3O_2)_2\ 100\ H_2O$.

II. *Lead.*

195. Two series of cells set up with electro-lead opposed to amalgamated zinc and electro-copper respectively, with acetate solutions uniformly of strength $\cdot 25\ M(C_2H_3O_2)_2\ 100\ H_2O$, gave the following results; the differences observed between the values obtained for different cells set up in the same way being notably greater than with most of the other combinations examined:—

	Zinc-Lead.	Lead-Copper.
Maximum	·616	·503
Minimum	·587	·471
Average	·608	·485
Probable error	±·0048	±·0044

---

[*] The acetate solutions employed were prepared by dissolving the freshly-precipitated, well-washed carbonates of the metals in boiling dilute acetic acid somewhat stronger than that required, filtering after cooling, and diluting to the proper extent.

From these average values the following valuations result for the voltaic constant for lead in acetate solution of strength $\cdot25\ Pb(C_2H_3O_2)_2\ 100\ H_2O$:—

Zinc-lead	. . . .	·608
Zinc-copper — Copper-lead	. . $\left\{ \begin{array}{c} 1\cdot091 \\ -\cdot485 \end{array} \right\}$	= ·606
	Mean	·607

Hence, since Thomsen finds that $Pb, O, 2C_2H_4O_2\,aq. = 65770$, the value of E_H is ·770, corresponding with 34940 gramme-degrees, whence

$$E - E_H = -\cdot163\ ;$$

i. e. the thermovoltaic constant for lead in acetate solution is negative, and of nearly the same magnitude as in nitrate solution, or in contact with lead sulphate suspended in zinc or cadmium-sulphate solution of corresponding strength, $\cdot25\ PbX\ 100\ H_2O$. In consequence the actual E.M.F. of a lead-copper-acetate cell *exceeds* that due to the net chemical change taking place therein, just as in lead-copper-sulphate and lead-copper-nitrate cells.

Some observations were made on the rate of depreciation in E.M.F. with increasing current-density in zinc-lead-acetate cells, with the result of showing that the average rate of fall is indicated by a curve lying between the analogous curves obtained with zinc-silver-sulphate and iron-copper-sulphate cells (§§ 130 and 176), being below the former and above the latter, which, as already shown, overlie the analogous curves obtained with zinc-copper-sulphate and zinc-cadmium-sulphate cells. It is remarkable, in this connection, that the thermovoltaic constants for the metals silver, lead, iron, copper, and cadmium in these solutions respectively follow in the same order as regards numerical magnitude, though not as regards sign:—

Silver (in sulphate solution) . .	−·351
Lead (in acetate solution) . .	−·163
Iron (in sulphate solution)	+·113 to +·148
Copper (in sulphate solution) .	+·009
Cadmium (in sulphate solution)	+·005 to −·010

III. *Silver.*

196. The following values were obtained with cells containing electro-silver immersed in saturated silver-acetate solution opposed to amalgamated zinc and electro-copper immersed in their respective acetate solutions, the constant strength being ·057 $M(C_2H_3O_2)_2$ 100 H_2O :—

	Zinc-Silver.	Copper-Silver.
Maximum	1·501	·404
Minimum	1·486	·389
Average	1·490	·397
Probable error	±·0024	±·0021

From these figures the following concordant valuations are deduced for the voltaic constant of electro-silver immersed in saturated silver-acetate solution :—

Zinc-silver		1·490
*Zinc-copper + Copper-silver	$\left\{ \begin{array}{r} 1·091 \\ + \ ·397 \end{array} \right\}$	=1·488
	Mean	1·489

The heat of formation of silver acetate not being known, the value of E_H cannot be calculated. Admitting that this value is the same as in the case of nitrate cells of the same molecular solution-strength, viz. near to 1·890, the value of $E - E_H$ would be $-$·401 ; whence it is at least evident that the thermovoltaic constant for electro-silver in acetate solution is a large negative quantity, comparable in magnitude with the corresponding constants found for sulphate and nitrate solutions.

It is noteworthy that the E.M.F. of lead-silver-acetate cells deduced from the foregoing experiments is 1·489 − ·607 = ·882 volt. On setting up a number of such cells, however, fluctuating and inconstant figures were obtained, usually averaging during the first half-hour after setting up values from ·02 to ·12 volt below this amount ; these cells therefore resembled in this respect the lead-copper-chloride cells above described (§ 184).

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* Assumed to be the same as the value found for solution-strength 25 $M(C_2H_3O_2)_2$ 100 H_2O.

E. *Voltaic and Thermovoltaic Constants of Metals immersed in Solutions of their Bromides.*

197. The experiments above described indicate that the sign and magnitude of the thermovoltaic constant for a given metal does not vary widely, whether the metal be in contact with its sulphate, nitrate, or acetate, whereas the values obtained under these circumstances are often considerably different from those obtained when in contact with its chloride. In order to trace out whether the different halogen salts exhibit analogy with these oxygen-acid salts, or whether they differ materially amongst themselves, a number of cells were examined containing various metals immersed in solutions of their respective bromides of constant strength $\cdot 25 MBr_2\ 100\ H_2O$, or in magmas of their bromides immersed in zinc-bromide solution of this strength (saving in the case of lead bromide, where the sparing solubility necessitated the use of weaker solutions).

I. *Cadmium.*

The following values were obtained with zinc-cadmium-bromide cells :—

Maximum	·319
Minimum	·311
Average	·315
Probable error	± ·0014

Julius Thomsen finds the values Zn, Br_2 aq. = 90960, and Cd, Br_2 aq. = 75640; whence $E_H = \cdot 338$, corresponding with 15320 gramme-degrees. Hence

$$E - E_H = -\cdot 023\ ;$$

that is, the thermovoltaic constant for electro-cadmium in bromide solution of strength $\cdot 25 CdBr_2\ 100\ H_2O$ is a small negative quantity, not quite so large numerically as that for the corresponding chloride solution (viz. $-\cdot 036$).

II. *Silver.*

☞ 198. The following values were obtained with cells set up with amalgamated zinc opposed to electro-silver immersed in a magma of freshly precipitated well-washed silver bromide suspended in zinc-bromide solution, the solution-strength throughout being $\cdot25 ZnBr_2\ 100\ H_2O$.

Maximum	·909
Minimum	·901
Average	·906
Probable error	±·0012

Julius Thomsen finds $Ag_2, Br_2 = 45400$; whence $E_H = 1{\cdot}005$, corresponding with 45560 gramme-degrees. Hence

$$E - E_H = -{\cdot}099\,;$$

that is, the thermovoltaic constant for silver in contact with silver bromide suspended in zinc-bromide solution is a notable negative quantity, slightly less numerically than the corresponding value for silver chloride suspended in equally strong zinc-chloride solution (viz. − 112).

III. *Lead.*

199. Two sets of cells were examined containing electro-lead immersed in saturated solution of lead bromide of strength $\cdot037\ PbBr_2\ 100\ H_2O$ opposed to amalgamated zinc and electro-cadmium immersed in their respective bromide solutions of the same strength. The following values were obtained :—

	Zinc-Lead.	Cadmium-Lead.
Maximum	·575	·257
Minimum	·567	·255
Average	·571	·256
Probable error	±·0014	±·0001

These figures lead to the following valuations for the voltaic constant of lead in saturated lead-bromide solution :—

Zinc-lead		·571
Zinc-cadmium* + Cadmium-lead . .	$\left\{\begin{matrix} 315 \\ +256 \end{matrix}\right\}$	= ·571
Mean		·571

---

* Zinc-cadmium assumed to give the same value for this solution-strength as that found above for the somewhat stronger solution $\cdot25 CdBr_2\ 100\ H_2O$.

Julius Thomsen finds Pb, Br_2 aq. = 54410; whence $E_H = \cdot 806$, corresponding with 36550 gramme-degrees. Hence

$$E - E_H = -\cdot 235\ ;$$

i. e. the thermovoltaic constant for electro-lead in saturated lead-bromide solution is a large negative quantity, slightly greater numerically than that for lead in saturated lead-chloride solution, viz. −·222.

IV. *Mercury.*

200. When mercuric-bromide solution is agitated with metallic mercury, mercurous bromide is rapidly formed, so that in a very short time practically all mercury and bromine are removed from solution, just as is the case with mercuric chloride (§ 183). Cells were therefore set up containing mercury in contact with a magma of mercurous bromide (freshly precipitated and well washed), suspended in zinc-bromide solution, and opposed, firstly, to amalgamated zinc immersed in zinc-bromide solution, and, secondly, to electro-silver in contact with a magma of silver bromide suspended in zinc-bromide solution, the solution-strength being $\cdot 25 ZnBr_2$ 100 H_2O throughout. The following values were obtained, the current passing, in the latter case, in the direction opposite to that predicable from the relative heats of formation of mercurous and silver bromides :—

	Zinc-Mercury.	Mercury-Silver.
Maximum	·974	−·062
Minimum	·969	−·073
Average	·972	−·066
Probable error	±·0006	±·0019

These figures lead to the following valuations for the voltaic constant of mercury in contact with mercurous bromide suspended in $\cdot 25 ZnBr_2$ 100 H_2O :—

Zinc-mercury		·972
Zinc-silver − Mercury-silver . .	$\left\{\begin{matrix} \cdot 906 \\ +\cdot 066 \end{matrix}\right\}$	= ·972
Mean		·972

Julius Thomsen finds $Hg_2,Br_2=68290$; whence $E_H=\cdot 500$ volt, corresponding with 22670 gramme-degrees. Hence

$$E-E_H=+\cdot 472\ ;$$

that is, the thermovoltaic constant for mercury in contact with this bromide magma is a large positive quantity, somewhat greater than that observed with the corresponding chloride magma, viz. $+\cdot 458$.

It is noticeable that the heat of formation of mercurous bromide exceeds that of lead-bromide solution (Hg_2, $Br_2=68290$, Pb, Br_2 aq.$=54410$, difference 13880, corresponding with ·306 volt); whilst the value of k_1-k_2 for lead-mercury-bromide cells is

$$-\cdot 235-(+\cdot 472)=-\cdot 707\ ;$$

so that $E_H+k_1-k_2$ is negative relatively to E_H, being $=-\cdot 401$. On examining various such cells (solution-strength $=\cdot 037MBr_2\ 100\ H_2O$), the E.M.F. was found to be actually of negative sign, the average observed value being $-\cdot 402$.

V. *Iron.*

201. A series of cells was examined containing plates of nearly pure sheet iron (bright) opposed to amalgamated zinc and electro-cadmium with bromide solutions of the respective metals of strength $\cdot 25MBr_2\ 100\ H_2O$ (the ferrous-bromide solutions being prepared by agitating together pure spongy iron in excess and weighed quantities of bromine and water in a stoppered bottle, filtering and using immediately). The following numbers were obtained :—

	Zinc-Iron.	Iron-Cadmium.
Maximum	·441	−·086
Minimum	·401	−·126
Average	·417	−·103
Probable error	±·005	±·005

As with the cadmium-iron sulphate and chloride cells, the current passed in the second case in the direction opposite to that predicable from the relative heats of formations of iron-

and cadmium-bromide solutions; while the E.M.F. actually set up in the first case notably *exceeded* that similarly calculable from the heats of formation of zinc- and iron-bromide solutions.

These numbers lead to the following valuations for the voltaic constant for bright iron in solution of strength $\cdot 25\,FeBr_2\,100\,H_2O$:—

Zinc-iron	·417
Zinc-cadmium − Cadmium-iron $\left\{\begin{matrix}\cdot 315\\ +\cdot 103\end{matrix}\right\}=$	·418
Mean . . .	·418

Julius Thomsen finds $Fe, Br_2\,aq. = 78070$; whence $E_H =$ ·284 volt, corresponding with 12890 gramme-degrees. Hence

$$E - E_H = +\cdot 134\,;$$

i. e. the thermovoltaic constant is a notable positive quantity, less, however, in magnitude than the corresponding value for ferrous-chloride solution of the same strength, viz. + ·204.

VI. *Aluminium.*

202. A number of cells were set up with bright aluminium plates opposed to amalgamated zinc and electro-cadmium, immersed in their respective bromide solutions of strength $\cdot 25\,MBr_2\,100\,H_2O$. The readings exhibited the same fluctuations as were observed with the sulphate and chloride cells previously examined (§ 178 and § 186). The following readings were obtained, the current passing in the opposite direction to that calculable from the relative heats of formation of zinc- and aluminium-bromide solutions in the first case, but in the normal direction in the second case :—

	Zinc-Aluminium.	Cadmium-Aluminium.
Maximum	− ·323	+ ·037
Minimum	− ·278	+ ·013
Average	− ·296	+ ·022
Probable error	± ·007	± ·005

These numbers lead to the following valuations for the voltaic constant for bright aluminium in bromide solution $\cdot 25\,Al_{\frac{2}{3}}Br_2\,100\,H_2O$:—

Zinc-aluminium	$+\cdot296$
Zinc-cadmium – Aluminium-cadmium $\left\{\begin{matrix}\cdot315\\-\cdot022\end{matrix}\right\}$	$=+\cdot293$
Mean	$+\cdot295$

the constant being of + sign, since aluminium actually acquires the higher potential, although it might *à priori* be expected to acquire the lower potential.

Julius Thomsen's thermochemical data lead to the value $Al_{\frac{2}{3}}, Br_2 aq. = 136680$; whence $E_H = -1{\cdot}008$ volt, corresponding with 45720 gramme-degrees. Consequently

$$E - E_H = +\cdot295 - (-1{\cdot}008) = +1{\cdot}303;$$

i. e. the thermovoltaic constant for bright aluminium in bromide solution $\cdot25\,Al_{\frac{2}{3}}Br_2\ 100\,H_2O$ is a large positive quantity, slightly greater than that found with the corresponding chloride solution, viz. $+1{\cdot}288$.

F. *Voltaic and Thermovoltaic Constants of Metals immersed in Solutions of their Iodides.*

I. *Cadmium.*

203. The following values were obtained with a number of cells set up with amalgamated zinc and electro-cadmium immersed in solutions of their iodides of strength $\cdot25\,MI_2\ 100\,H_2O$:—

Maximum	·326
Minimum	·320
Average	·322
Probable error	±·0008

Julius Thomsen finds the heat-values for this strength of solution are $Zn, I_2, aq. = 60540$, and $Cd, I_2, aq. = 47870$; whence $E_H = \cdot279$ volt, corresponding with 12670 gramme-degrees. Hence $E - E_H = +\cdot043$; *i. e.* the thermovoltaic constant for cadmium in iodide solution of strength $\cdot25\,CdI_2\ 100\,H_2O$ is positive in sign but not large numerically. It is noteworthy that, with the corresponding bromide and chloride solutions, the values were negative, viz. $-\cdot023$ and $-\cdot036$ respectively; the bromide value being thus intermediate between the chloride and iodide values.

II. *Silver.*

204. The following numbers were obtained with cells set up with electro-silver immersed in a magma of freshly precipitated well-washed silver iodide suspended in zinc-iodide solution, and opposed to amalgamated zinc or electro-cadmium in their respective iodide solutions, the solution-strength being uniformly ·25 MI_2 100 H_2O.

	Zinc-Silver.	Cadmium-Silver.
Maximum	·713	·393
Minimum	·696	·374
Average	·7055	·384
Probable error	±·0028	±·0030

These values lead to the following valuations of the voltaic constant for electro-silver in contact with this magma :—

$$\text{Zinc-silver} \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad \cdot 7055$$

$$\text{Zinc-cadmium} + \text{Cadmium-silver} \left\{ \begin{array}{r} \cdot 322 \\ + \cdot 384 \end{array} \right\} = \cdot 706$$

$$\text{Mean} \; . \; . \; . \; . \qquad \overline{\cdot 736}$$

Since Thomsen finds $Ag_2, I_2 = 27600$, the value of E_H is ·726 volt, corresponding with 32940 gramme-degrees : hence $E - E_H = - \cdot 020$.

On comparing this value with those found for silver bromide suspended in zinc-bromide solution and for silver chloride suspended in zinc-chloride solution, all of the same strength ·25 ZnX_2 100 H_2O, viz. $-\cdot 099$ and $-\cdot 112$ volt respectively, it is noticeable that the direction of variation is the same as that observed in the analogous cases for cadmium, the bromide value being intermediate between the chloride and iodide values, the last being algebraically the greatest.

III. *Mercury.*

205. Cells were set up with mercury in contact with freshly precipitated mercurous iodide suspended in zinc-iodide solution, and opposed, firstly, to amalgamated zinc in zinc-iodide solution, and, secondly, to electro-silver immersed in a magma of freshly precipitated silver-iodide and zinc-iodide solution, the solution-strength being uniformly ·25 ZnI_2 100 H_2O. The following values were obtained :—

	Zinc-Mercury.	Mercury-Silver.
Maximum	·806	−·092
Minimum	·797	−·101
Average	·800	−·096
Probable error	±·0013	±·0014

the current passing in the latter case in the direction opposite to that predicable from the relative heats of formation of silver and mercurous iodides. From these values the following valuations result for the voltaic constant of mercury in contact with mercurous iodide suspended in $\cdot 25\ ZnI_2\ 100\ H_2O$:—

$$\begin{array}{lr} \text{Zinc-mercury} \quad . \ . \ . \ . \ . \ . \ . \ . & \cdot 800 \\ \text{Zinc-silver} - \text{Mercury-silver} \left\{ \begin{array}{r} \cdot 706 \\ + \cdot 096 \end{array} \right\} & \cdot 802 \\ \hline \text{Mean} \quad . \ . \ . & \cdot 801 \end{array}$$

Julius Thomsen finds that $Hg_2, I_2 = 48440$; whence $E_H =$ ·267 volt, corresponding with 12100 gramme-degrees. Hence $E - E_H = + \cdot 534$; *i.e.* the thermovoltaic constant for mercury in contact with a magma of mercurous iodide suspended in $\cdot 25\ ZnI_2\ 100\ H_2O$ is a large positive quantity, as similarly found for mercury in contact with mercurous-bromide and zinc-bromide solution and with mercurous-chloride and zinc-chloride solution of the same solution-strength, these latter two values being respectively +·472 and +·458. So that the bromide value is intermediate between the values for chloride and iodide; whilst the direction of variation with the three halogens is the same as that observed both with cadmium and with silver, viz. that the iodide value is algebraically the greatest.

IV. *Lead.*

206. The very sparing solubility of lead iodide rendered it impracticable to obtain good readings with cells set up with aqueous solutions of that salt. Accordingly a magma of lead-iodide and zinc-iodide solution of strength $\cdot 25\ ZnI_2\ 100\ H_2O$ was employed to surround the electro-lead plates used, opposed in one set of experiments to amalgamated zinc in the same zinc-iodide solution, and in another set to mercury immersed in a magma of mercurous iodide suspended in the same zinc-

iodide solution. The following values were obtained, the degree of concordance being distinctly less than with most of the other combinations examined :—

	Zinc-Lead.	Lead-Mercury.
Maximum	·489	−·317
Minimum	·418	−·379
Average	·455	−·347
Probable error	±·009	±·008

The lead-mercury cells gave a current in the direction opposite to that deducible from the relative heats of formation of zinc and mercurous iodides.

From these numbers the following valuations of the voltaic constant result :—

$$\text{Zinc-lead} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \cdot455$$

$$\text{Zinc-mercury} + \text{Mercury-lead} \left\{ \begin{array}{r} \cdot801 \\ -\cdot347 \end{array} \right\} = \cdot454$$

$$\text{Mean} \quad . \quad . \quad . \quad . \quad \cdot455$$

Julius Thomsen finds $Pb, I_2 = 39800$; whence $E_H = \cdot457$. Hence the thermovoltaic constant for electro-lead immersed in a magma of lead iodide suspended in $\cdot25\ ZnI_2\ 100\ H_2O$ is a minute negative quantity, viz. $-\cdot002$.

This value and those above found for electro-lead in contact with saturated-chloride and bromide-of-lead solutions respectively, viz. $-\cdot222$ and $-\cdot235$, are not strictly comparable, since the solution-strength was not the same throughout ; whilst a magma containing zinc-iodide solution was used for the iodide cells and pure lead-salts for the others, which, moreover, had respectively the strengths $\cdot05\ PbCl_2\ 100\ H_2O$, and $\cdot037\ PbBr_2\ 100\ H_2O$. Probably from these causes the bromide value is not intermediate between the chloride and iodide values, as might have been anticipated ; but the last value is algebraically the greatest, as was found with cadmium-silver and mercury.

It is hence evident that whilst the thermovoltaic constants of metals in contact with their oxy salts (sulphates, nitrates, and acetates) do not vary widely, the same remark is not true for their halogen salts (chlorides, bromides, iodides). In general the thermovoltaic constant is decreased (algebraically) by substitution of bromide for iodide or of chloride for bromide; although this rule is not without exception, *e. g.* in the case of iron, where the values for ·25 FeX_2 100 H_2O are +·204 and +·134, where X represents chlorine and bromine respectively, the substitution of chlorine for bromine thus causing a notable *increase.*

Summary of Results.

207. The experiments above described lead to the general conclusion that electromotors, consisting of voltaic cells in which two different metals are surrounded by solutions of corresponding salts respectively, are capable of generating electromotive forces which (when not depreciated sensibly below their maximum value by giving rise to currents of densities greater than certain small limiting values) usually *stand in no simple relationship to the chemical action taking place in the cell* during the passage of the currrent, or to the heat-evolution taking place during that passage, or to the heats of formation of the two solutions electrolyzed. The values of the maximum E.M.F.'s thus generated may, however, be deduced within very close limits of accuracy by taking the algebraic difference between certain numerical values or *voltaic constants* assigned to each metal in contact with each given solution, these values varying slightly according to the surface-nature of the immersed metal, and being also dependent on the nature and strength of the solution of metallic salt in contact with the metal, and probably also varying with the temperature, but being otherwise actually constant.

Further, these maximum E.M.F. values may be connected with the difference in heat of formation between the two solutions electrolyzed by supposing that *the total difference of potential set up is due to two superposed causes*:—one, the heat-evolution due to the difference in heat of formation of the two solutions, which tends to make the metal immersed in the electrolyte of lesser formation-heat acquire the higher potential (like the copper plate of a Daniell cell); the other, a *thermo-voltaic* action akin to the *modus operandi* of an ordinary thermovoltaic couple, in virtue of which a difference of potential is set up expressible by the algebraic difference between two numerical values, or *thermovoltaic constants*, assignable to each metal respectively, the which values vary *pari passu* with the variations in the corresponding voltaic constants. This thermovoltaic action being expressible by $k_1 - k_2$, and the first source of potential-difference being indicated by E_H, the total difference of potential set up is

$$E = E_H + k_1 - k_2,$$

where, if $k_1 - k_2$ be materially different from zero (which is most frequently the case), the value of E will differ materially from that of E_H, exceeding or falling short of it according as $k_1 - k_2$ is positive or negative in sign with respect to E_H. In the latter case, if $k_1 - k_2$ be numerically greater than E_H, the direction of the current actually generated is the reverse of that predicable from the relative heats of formation of the electrolytes.

208. The following Table furnishes a brief epitome of the mean values of the voltaic and thermovoltaic constants deduced above for various metals and fluids at a temperature within a very few degrees above or below 18° C.; the solutions surrounding both plates being of equal strength (*m* zinc-salt molecules per 100 water molecules), the plate-surfaces being freshly amalgamated ones for zinc (standard), bright fused metal for iron, magnesium, and aluminium, and freshly electro-coated plates in all other cases.

Metal.	Surrounding Fluid.	*m*.	Voltaic constant.	E_H.	Thermovoltaic constant.
COPPER	Sulphate	·1 to 2·25	1·114 invariable.	1·105 invariable.	+·009
	Nitrate	·25 to 8·0	1·066 to 1·109	1·105 to 1·100	−·039 to +·005
	Acetate	·25	1·091	1·111	−·020
	Chloride: Cu_2Cl_2 suspended in $CuCl_2$ solution; or $CuCl_2$ solution alone	·25	1·099	1·038	+·061
	Chloride: Cu_2Cl_2 suspended in $CdCl_2$ solution.	·25	1·001		−·037
	Chloride: Cu_2Cl_2 suspended in $ZnCl_2$ solution.	·25	·988		−·050
CADMIUM	Sulphate	·1 to 5·0	·362 to ·357	·357 to ·367	+·005 to −·010
	Nitrate	·25	·352	·357	−·005
	Chloride	·25 to 8·0	·330 to ·262	·366 to ·240	−·036 to +·045
	Bromide	·25	·315	·338	−·023
	Iodide	·25	·322	·279	+·043

Table (*continued*).

Metal.	Surrounding Fluid.	*m*.	Voltaic constant.	E'_H.	Thermovoltaic constant.
SILVER	Sulphate	·042	1·539	1·890	−·351
	Nitrate	·25 to 2·0	1·495 to 1·556	1·890	−·395 to −·334
	Acetate	·057	1·489	?	Probably near to −·40
	Chloride: AgCl suspended in $ZnCl_2$ solution.	·25 to 6·0	1·080 to 1·014	1·192 to 1·076	−·112 to −·062
	Chloride: AgCl suspended in $CdCl_2$ solution.	·25	1·089	1·192	−·103
	Chloride: AgCl suspended in $CuCl_2$ solution.	·25	1·137		−·055
	Bromide: AgBr suspended in $ZnBr_2$ solution.	·25	·906	1·005	−·099
	Iodide: AgI suspended in ZnI_2 solution	·25	·706	·726	−·020
LEAD	Sulphate: $PbSO_4$ suspended in $ZnSO_4$ solution.	·1 to 5·0	·536 to ·487	·712 to ·704	−·176 to −·217
	Sulphate: $PbSO_4$ suspended in $CdSO_4$ solution.	·1 to 5·0	·550 to ·505		−·162 to −·199
	Nitrate	·25 to 2·0	·580 to ·591	·759 to ·716	−·179 to −·125
	Acetate	·25	·607	·770	−·163
	Chloride	·05	·591	·813	−·222
	Bromide	·037	·571	·806	−·235
	Iodide: PbI_2 suspended in ZnI_2 solution	·25	·455	·457	−·002
IRON	Sulphate	0·1 to 1·0	·432 to ·398	·284	+·148 to +·114
	Chloride	·25	·488	·284	+·204
	Bromide	·25	·418	·284	+·134
MERCURY	Sulphate: Hg_2SO_4 suspended in $ZnSO_4$ solution.	·1 to 5·75	1·457 to 1·514	?	Probably near +·25 to +·30
	Nitrate (mercurous)	·25	1·499	1·202	+·297
	Chloride: Hg_2Cl_2 suspended in $HgCl_2$ solution.	·25	1·257	·668	+·589
	Chloride: Hg_2Cl_2 suspended in $CdCl_2$ solution.	·25	1·141		+·473
	Chloride: Hg_2Cl_2 suspended in $ZnCl_2$ solution.	·25 to 9·5	1·123 to ·988	·668 to ·536	+·455 to +·481
	Bromide: Hg_2Br_2 suspended in $ZnBr_2$ solution	·25	·972	·500	+·472
	Iodide: Hg_2I_2 suspended in ZnI_2 solution	·25	·801	·267	+·534
MAGNESIUM.	Sulphate	1·0	−·725	−1·634	+·909
	Nitrate	·25	−·530	−1·631	+1·101
	Chloride	·25	−·701	−1·634	+·933
ALUMINIUM	Sulphate	·5	+·537	−·982	+1·519
	Chloride	·25	+·280	−1·008	+1·288
	Bromide	·25	+·295	−1·008	+1·303

209. The following is a list of the cells examined, in which the value of $k_1 - k_2$ is opposite in sign to, and numerically greater than, E_H; so that the current actually generated *flows in the direction opposite to that predicable from the relative heats of formation of the electrolytes*:—

Combination.	*m.*	E.	E_H.	$E - E_H = k_1 - k_2$.
Iron-cadmium-sulphate ...	0·1 to 1·0	− ·073 to − ·035	+ ·075	− ·110 to − ·148
Iron-cadmium-chloride ...	·25	− ·157	+ ·082	− ·239
Iron-cadmium-bromide ...	·25	− ·103	+ ·054	− ·157
Zinc-aluminium-sulphate ...	·5	+ ·537	− ·982	+ 1·519
Zinc-aluminium-chloride ...	·25	+ ·280	− 1·008	+ 1·288
Zinc-aluminium-bromide ...	·25	+ ·296	− 1·008	+ 1·304
Copper-silver-chloride. AgCl suspended in $ZnCl_2$ solution	·25	− ·020	+ ·154	− ·174
Copper-silver-chloride. AgCl suspended in $CdCl_2$ solution	·25	− ·010		− ·164
Mercury-silver-nitrate	·25	− ·004	+ ·688	− ·692
Mercury-silver-chloride. Both suspended in $ZnCl_2$	·25	− ·046	+ ·525	− ·571
Mercury-silver-bromide. Both suspended in $ZnBr_2$	·25	− ·066	+ ·505	− ·571
Mercury-silver-iodide. Both suspended in ZnI_2	·25	− ·096	+ ·460	− ·556
Mercury-silver-chloride. AgCl suspended in $ZnCl_2$ Hg_2Cl_2 ,, $CdCl_2$	·25	− ·058	+ ·525	− ·583
Mercury-silver-chloride. AgCl suspended in $CdCl_2$ Hg_2Cl_2 ,, $ZnCl_2$	·25	− ·038		− ·563
Mercury-silver-chloride. Both suspended in $CdCl_2$	·25	− ·050		− ·575
Mercury-silver-chloride. AgCl suspended in $ZnCl_2$ Hg_2Cl_2 ,, $HgCl_2$	·25	− ·167		− ·692
Lead-mercury-chloride. Hg_2Cl_2 suspended in $CdCl_2$	·05	− ·549	+ ·145	− ·694
Lead-mercury-chloride. Hg_2Cl_2 suspended in $ZnCl_2$	·05	− ·539		− ·684
Lead-mercury-bromide. Hg_2Br_2 suspended in $ZnBr_2$	·037	− ·402	+ ·306	− ·708
Lead-mercury-iodide. Both suspended in ZnI_2	·025	− ·347	+ ·190	− ·537

210. The following is a list of the cells examined in which the value of $k_1 - k_2$ is of the same sign as E_H; so that the E.M.F. actually set up *exceeds* in numerical value that predicable from the relative heats of formation of the electro-

lytes; only those cells are named where the excess is somewhat considerable, *i. e.* 0·1 volt or upwards.

Combination.	*m.*	E.	E_H.	Excess.
Lead-copper-sulphate. $PbSO_4$ suspended in $ZnSO_4$ solution	0·1 to 2·0	·577 to ·611	·393 to ·394	+·184 to +·217
Lead-copper-sulphate. $PbSO_4$ suspended in $CdSO_4$ solution	0·1 to 2·0	·564 to ·596		+·171 to +·202
Lead-copper-nitrate	·25 to 2·0	·486 to ·519	·345 to ·388	+·141 to +·128
Lead-copper-acetate	·25	·485	·341	+·144
Lead-copper-chloride	·05	Irregular, about ·475	·225	About +·25
Zinc-iron-sulphate	0·1 to 1·0	·445 to ·399	·284	+·161 to +·115
Zinc-iron chloride	·25	·490	·284	+·206
Zinc-iron-bromide	·25	·417	·284	+·133
Zinc-mercury-sulphate	·1 to 5·75	1·514 to 1·457	?	Probably about +·3
Zinc-mercury-nitrate	·25	1·500	1·202	+·298
Zinc-mercury-chloride. Hg_2Cl_2 suspended in $HgCl_2$ solution	·25	1·256	·668	+·588
Zinc-mercury-chloride. Hg_2Cl_2 suspended in $CdCl_2$ solution	·25	1·140		+·572
Zinc-mercury-chloride. Hg_2Cl_2 suspended in $ZnCl_2$ solution	·25 to 9·5	1·123 to ·988	·668 to ·536	+·452 to +·481
Zinc-mercury-bromide. Hg_2Br_2 suspended in $ZnBr_2$ solution	·25	·972	·500	+·472
Zinc-mercury-iodide. Hg_2I_2 suspended in ZnI_2 solution	·25	·800	·267	+·533
Cadmium-mercury-chloride. Hg_2Cl_2 suspended in $HgCl_2$ solution	·25	·929	·302	+·627
Cadmium-mercury-chloride. Hg_2Cl_2 suspended in $CdCl_2$ solution	·25	·812		+·510
Cadmium-mercury-chloride. Hg_2Cl_2 suspended in $ZnCl_2$ solution	·25	·799		+·497
Copper-mercury-nitrate	·25	·433	·097	+·336
Lead-mercury-nitrate	·25	·917	·443	+·474
Lead-silver-chloride. AgCl suspended in $ZnCl_2$ solution	·05	·489	·379	+·110
Lead-silver-chloride. AgCl suspended in $PbCl_2$ solution	·05	·480		+·101

211. The following is a list of the cells examined in which the value of $k_1 - k_2$ is of the opposite sign to, but not greater in magnitude than, E_H; so that the E.M.F. actually set up is

less in numerical value than that predicable from the relative heats of formation of the electrolytes ; only those cells are named where the deficiency is somewhat considerable, viz. 0·1 volt and upwards.

Combination.	*m.*	E.	E_H.	Deficiency.
Zinc-silver-sulphate	·042	1·536	1·890	·354
Zinc-silver-nitrate	·25 to 2·0	1·495 to 1·556	1·890	·395 to ·364
Zinc-silver-acetate	·057	1·490	?	Probably near ·40
Zinc-silver-chloride. $AgCl$ suspended in $ZnCl_2$ solution	·25 to 6·0	1·080 to 1·014	1·192 to 1·076	·116 to ·062
Zinc-silver-chloride. $AgCl$ suspended in $CdCl_2$ solution	·25	1·088	1·192	·104
Copper-silver-sulphate	·042	·4235	·785	·3615
Copper-silver-nitrate	·25 to 2·0	·429 to ·446	·785 to ·786	·356 to ·340
Copper-silver-acetate	·057	·397	?	Probably about ·39
Copper-silver-chloride. $AgCl$ suspended in $CuCl_2$ solution	·25	·035	·154	·119
Cadmium-silver-sulphate	·042	1·1805	1·533	·3525
Zinc-lead-sulphate. $PbSO_4$ suspended in $ZnSO_4$ solution	·1 to 5·0	·537 to ·487	·712 to ·704	·175 to ·217
Zinc-lead-sulphate. $PbSO_4$ suspended in $CdSO_4$ solution	·1 to 5·0	·550 to ·505		·162 to ·199
Zinc-lead-nitrate	·25 to 2·0	·580 to ·591	·759 to ·716	·179 to ·125
Zinc-lead-acetate	·25	·608	·770	·162
Zinc-lead-chloride	·05	·591	·813	·222
Zinc-lead-bromide	·037	·571	·806	·235
Cadmium-lead-sulphate	·1 to 3·0	·173 to ·133	·355 to ·345	·182 to ·212
Cadmium-lead-chloride	·05	·260	·447	·187
Cadmium-lead-bromide	·037	·256	·468	·212
Lead-silver-sulphate. $PbSO_4$ in $ZnSO_4$ solution	·042	1·003	1·1775	·1745
Lead-silver-nitrate	·25 to 2·0	.914 to ·965	1·131 to 1·174	·217 to ·207
Lead-silver-acetate	·037	Irregular, about 0·8	?	Probably about ·3
Iron-lead-sulphate. $PbSO_4$ suspended in $ZnSO_4$ solution	·1 to 1·0	·120 to ·112	·428	·308 to ·316
Iron-copper-sulphate	·1 to 1·0	·685 to ·715	·821	·136 to ·106
Iron-silver-sulphate	·042	1·103	1·605	·502
Iron-silver-chloride. $AgCl$ in $ZnCl_2$ solution	·25	·592	·908	·316
Zinc-magnesium-sulphate	1·0	·724	1·634	·910
Zinc-magnesium-nitrate	·25	·531	1·631	1·100
Zinc-magnesium-chloride	·25	·702	1·634	·932
Copper-magnesium-sulphate	1·0	1·840	2·739	·899
Copper-magnesium-nitrate	·25	1·595	2·736	1·141
Cadmium-magnesium-chloride	·25	1·030	2·000	·970
Aluminium-copper-sulphate	·5	·578	2·087	1·509
Aluminium-cadmium-chloride	·25	·050	1·374	1·324
Aluminium-cadmium-bromide	·25	·022	1·346	1·324

212. The following is a list of the cells examined in which the value of k_1-k_2 is not numerically greater than E_H, and lies within the limits $\pm 0{\cdot}1$ volt. It is evident that the number of cells coming into this category is only a fraction of the total number of combinations examined.

Combination.	*m.*	E.	E_H.	Differences.
Zinc-copper-sulphate	·25 to 2·25	1·114 invariable	1·105 invariable	+·009
Zinc-copper-nitrate	·25 to 8·0	1·066 to 1·091	1·105 to 1·100	+·005 to −·039
Zinc-copper-acetate	·25	1·091	1·111	−·020
Zinc-copper-chloride. Cu_2Cl_2 suspended in $CuCl_2$ sol., or $CuCl_2$ sol. alone...	·25	1·0985	1·038	+·061
Zinc-copper-chloride. Cu_2Cl_2 suspended in $CdCl_2$ solution	·25	1·001		−·037
Zinc-copper-chloride. Cu_2Cl_2 suspended in $ZnCl_2$ solution	·25	·988		−·050
Zinc-cadmium-sulphate	·1 to 5·0	·362 to ·357	·357 to ·367	+·005 to −·010
Zinc-cadmium-nitrate	·25	·351	·357	−·006
Zinc-cadmium-chloride	·25 to 8·0	·330 to ·262	·366 to ·240	−·036 to +·045
Zinc-cadmium-bromide	·25	·315	·338	−·023
Zinc-cadmium-iodide	·25	·322	·279	+·043
Copper-cadmium-sulphate ...	·1 to 2·0	·752 to ·755	·743 to ·748	+·909 to +·007
Copper-cadmium-nitrate......	·25	·713	·748	−·035
Copper-cadmium-chloride. Cu_2Cl_2 in $CuCl_2$ sol., or $CuCl_2$ sol. alone	·25	·769	·672	+·097
Copper-cadmium-chloride. Cu_2Cl_2 in $CdCl_2$ solution .	·25	·671		−·001
Copper-cadmium-chloride. Cu_2Cl_2 in $ZnCl_2$ solution .	·25	·659		−·013
Zinc-silver-chloride. AgCl in $CuCl_2$ solution ...	·25	1·136	1·192	−·056
Zinc-silver-bromide. AgBr in $ZnBr_2$ solution...	·25	·906	1·005	−·099
Zinc-silver-iodide. AgI in ZnI_2 solution	·25	·7055	·726	−·0205
Cadmium-silver-chloride. AgCl in $CuCl_2$ sol.	·25	·807	·826	−·019
Cadmium-silver-chloride. AgCl in $CdCl_2$ solution ...	·25	·761		−·065
Cadmium-silver-chloride, AgCl in $ZnCl_2$ solution ...	·25	·751		−·075
Cadmium-silver iodide. AgI in ZnI_2 solution	·25	·384	·447	−·063
Zinc-lead-iodide. PbI_2 in ZnI_2 solution......	·25	·455	·457	−·002

XXIV. *A Capillary Multiplier.*

By A. M. Worthington, *M.A.**

[Plate XIV. figs. 1 & 2.]

This little instrument (Plate XIV. fig. 1) consists simply of a rectangular strip of platinum foil of known length rolled into a cylindrical coil, whose successive convolutions are kept separate at a distance of about 2 mm. by means of a strip of glass beads in the upper portion of the coil. The lower edges of all the convolutions are in the same plane; and the instrument when in use hangs from one end of a balance-beam with this plane horizontal.

The liquid whose surface-tension is to be determined is placed below the coil in a vessel which can be raised till the free surface touches the base of the coil. The pull now exerted on the coil is measured by weights placed in the other pan; and these weights afford, when certain precautions shortly to be mentioned are taken, an accurate measure of the surface-tension of the liquid.

The method is really that used twenty years ago by Wilhelmy†, and more recently by M. Dupré ‡, who, however, employed only a single cylindrical sheet of platinum instead of a coil, and an hydrometer instead of a balance for measuring the pull.

The only novelty lies in the substitution of the coil for the single sheet, by which the sensitiveness of the method is increased many-fold.

The principles involved may be briefly explained as follows: When any liquid is placed in a vessel whose sides it wets, *i. e.* against which the edge-angle of the liquid is 0°, the liquid is raised round the edge above the level of the free surface, and the weight of liquid so raised is equal to the surface-tension of the liquid multiplied by the periphery across which the surface-tension acts. When the periphery (p) is known and the weight (w) of liquid raised is known, then the tension per unit of length is known to be $\frac{w}{p}$.

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* Read November 22, 1884.

† Poggendorff's *Annalen*, 1863, No. 6, p. 177.

‡ See *Théorie mécanique de la Chaleur*, par M. A. Dupré (Paris, 1869) p. 245 *et seq.*

When a capillary tube is used for measuring the surface-tension, the periphery across which the force acts is the internal perimeter of the tube, and this is too small to be capable of very exact measurement; while the weight of liquid raised is that of a column whose height can indeed be accurately measured, but whose sectional area is again too small to be very correctly determined.

If a very wide tube be used, the perimeter can be measured with much greater accuracy; but the weight of liquid raised cannot now be determined in the same way as before, since the volume included between the surface of the meniscus and a horizontal plane touching its lowest point is now an important part of the whole volume raised. But the weight of the liquid raised along both the inside and outside perimeters of the tube is equal to the reactionary pull downwards of the liquid on the tube and may be determined by measuring this latter.

M. Dupré's wide cylinder of platinum foil was simply a tube whose inner and outer perimeters were sensibly equal and accurately known, and the pull across this perimeter could be determined in the way described.

The great advantage of the coil over the single sheet is that the periphery across which the tension acts may be made very great, while the diameter of the coil, and consequently the quantity of liquid required and the area of its exposed surface, remains small.

Thus one of my coils is made of a strip 50 centim. long and presents a perimeter of 1 metre, while its diameter is only 3 centim., and the pull of water on this is about 8 grams.

The beads of which the strip is composed for separating the convolutions are made of hard glass, and strung on fine platinum wire, so that the instrument may be very readily cleaned by heating to a bright heat in the Bunsen flame. The beads should not reach within 2 or 3 centim. of the lower edge of the coil, in order that the liquid which rises between the convolutions may not reach so high as to wet the glass. If the consecutive coils are 2 millim. apart, then water (which is raised higher than any other known liquid) will attain a height of about ·8 centim. But since the coil is liable to be dragged down into the liquid, it is well to leave an ample margin.

If the coil dips below the plane surface of the liquid, there is a correction necessary on account of the buoyancy of the liquid. If, on the other hand, the base of the coil is raised above the free surface, there is a traction to correct for, due to the adhesion of the liquid to the horizontal section of the spiral edge. By adjusting the level of the liquid-surface after it has wetted the coil to the level of the base of the coil, when the balance-beam is horizontal, the necessity for these corrections is avoided. The thickest foil that I use is ·0025 centim. thick, and the correction due to an error of adjustment of the surface, amounting to 1 millim., would, in a measure of the surface-tension of alcohol, amount to $\frac{1}{260}$ of the whole ; and it is easy to make the adjustment within much narrower limits than 1 millim.

Method of Use.

In order to prevent the coil from being dragged below the surface, or, on the other hand, separated from it, I find it convenient to fix two stops A and B (see fig. 2), just above and below the beam of the small unmounted balance that I employ : two stout pins stuck in a cork that is held in its place by a rod (as in the figure) serve the purpose very well.

After cleaning the coil in the Bunsen flame, adjusting its base so as to be horizontal by means of the three suspending cords, which are made of silk and are provided with beads through which the silk forms nooses like a tent-rope, and accurately counterpoising, a block C is placed below the right-hand pan at such a height that the pan rests on it when the beam is horizontal. Then the liquid to be tested is placed in a thin beaker, which stands on a small table, whose height can be easily adjusted by a ratchet-screw (the end of an optical lantern with a card on the top does very well). This is raised till the platinum is wetted, when it is at once drawn as far below the surface (4 or 5 millim.) as the position of the stop A will permit. The pan D is now pressed down by hand on the block C and held there, while the level of the liquid surface is adjusted to the base of the coil. Then D is released, C removed, and weights added to restore equilibrium.

It will be observed that the coil is, by the process of putting on the weights, gradually drawn out of the liquid, so that the topmost element of the elevated liquid will everywhere be in contact with a portion of the coil that has been thoroughly wetted, which will with most liquids reduce the contact-angle to zero.

A few points may be usefully mentioned about the construction of the coil. To make the strip of glass beads I use combustion-tubing drawn out to a diameter of about 2 millim. and cut first into lengths of about 20 centim. Out of a number of such pieces, a careful selection is made of those of most uniform thickness; these are then accurately cut to a length of about 2 centim., and of the beads thus made the strip is put together by passing through each in turn in opposite directions the two ends of a fine platinum wire (size no. 36). The smoothness of the glass strip allows the platinum coil to slide within it, so that by gentle pressure against a hard plane surface the edges of the convolutions can at any time be very accurately adjusted to the same plane. Other forms might doubtless be given to the multiplier, but the cylindrical coil is the most compact and requires for its use the smallest amount of liquid. The labour of double-threading the long strip of beads is considerable, and I have tried to avoid it by substituting a strip of asbestos cardboard, which would allow the coil to be cleansed by the action of the flame as before. But though in other respects satisfactory, the asbestos very rapidly gains in weight through the absorption of the vapour of many liquids, and cannot therefore be used unless wrapped in very thin platinum foil; but when so wrapped it is troublesome to coil, and does not allow the same ready adjustment of the edges of the coil to one plane.

Clifton College, Bristol,
October 16, 1884.

XXV. *Note on a Point in the Theory of Pendent Drops.*

By A. M. Worthington, *M.A.* *

[Plate XIV. figs. 3–5.]

In a paper on Pendent Drops (Proc. Roy. Soc. no. 214, 1881) I explained how, from a tracing of the outline of a drop pendent from a circular base, the value of the surface-tension of the liquid could be deduced with an accuracy that compared favourably with that of any other method.

The most difficult part of the process is the measurement at various levels of the inclination of the tangent of the curve to the axis; and I find that this difficulty does not disappear, as I hoped it might, when a photograph of the magnified image of the drop is substituted for a tracing made by hand.

It is essential to the success of the method to measure this inclination at levels where the horizontal sectional area of the drop is widely different. Thus in a drop shaped as in fig. 3 Plate XIV. it would be desirable to measure the inclination, say, at the level AB and again at the level CD. Now at AB, where the inclination changes very slowly, its value may be very accurately determined; but at CD the change of inclination is rapid and its determination difficult.

It has lately occurred to me that the necessity of finding the value of the inclination at more than one level may be avoided, while that level may be so chosen that the tangent is there vertical or changes its inclination very slowly.

Let ADCE (fig. 4) represent a horizontal circular section of the pendent drop taken at any level; ABC the generating curve in the plane of the paper; DBE the same curve in a plane at right angles to the paper. Consider first the equilibrium as regards vertical forces of the mass of liquid below the plane section. We may equate the vertical component of the surface-tension (T) round the circumference ADCE, to the weight (W) of the liquid below the section + the pressure on the area ADCE; so that, signifying by x the unknown distance of this section from the level of the free surface of the liquid, and by Δ the weight of unit volume of the liquid, we have

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* Read November 22, 1884.

$$T \cos\theta \times \pi\overline{AC} = W + \pi\overline{AO}^2 x\Delta \;. \quad . \quad . \quad . \quad \text{(i.)}$$

Again, if we consider the equilibrium, as regards horizontal forces parallel to the plane of the paper, of the mass ABDOE, we see that the surface-tension acting horizontally round the periphery DBE is equal to the hydrostatic pressure on the area DBE + the sum of the tensions across each element of the semicircumference DAE, each resolved first horizontally and then normally to DE. Now the hydrostatic pressure is equal to the area DBE × density of liquid × depth of the centre of gravity G of the area below the level of the free surface, and this depth $= OG + x$; and I have found that OG can be determined with great accuracy by cutting the figure out of carefully selected writing-paper, and balancing; again the sum of the horizontal tensions across the semicircumference resolved normally to $DE = T \sin\theta\overline{DE}$; so that

$$T \times \text{length } DBE = T \sin\theta\overline{DE} + \text{area } DBE\ (CG + x)\ \Delta,$$

or

$$T(\text{length } ABC - AC \sin\theta) = \text{area } ABC\ (OG + x)\Delta\,; \quad \text{(ii.)}$$

and from these two equations x can be eliminated and T found.

Now the section can be chosen at a place of contrary flexure, where the value of $\cos\theta$ can be obtained with very great accuracy; or, again, if the circular base from which the drop depends be small enough the drop will assume the form shown in fig. 5, in which at a certain level MN the curve is vertical, and $\sin\theta = 0$. When this is the case equation (i.) becomes

$$T \times \pi AC = W + \pi AO^2 x\Delta, \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

while (ii.) becomes

$$T \times ABC = \text{area } ABC(OG + x)\,\Delta. \quad . \quad . \quad \text{(iv.)}$$

The method here shown of considering separately the equilibrium first of vertical and then of horizontal forces is equally applicable to sessile drops and to portions of liquid raised by adhesion to a base, and brings out very clearly many results which have hitherto usually been obtained as special cases by rather complicated processes of integration.

Clifton College, Oct. 27, 1884.

XXVI. *The Influence of an Electric Current in Modifying the Rate of Thinning of a Liquid Film.* *By* Prof. A. W. Reinold, *F.R.S., and* Prof. A. W. Rücker, *F.R.S.*[*]

In 1877 the results of some experiments made by us on liquid films were published in the Proceedings of the Royal Society (Proc. Roy. Soc., No. 182, 1877). One object of the investigation was the determination of the electrical resistance of the films. The method of Wheatstone's Bridge was employed for this purpose, and the current was passed through a film only at the moment when an observation was required. Under these circumstances the films generally thinned until they became black; and we succeeded in obtaining several measures of their resistance when this colour was displayed. Subsequently this method was abandoned for another, in which continuous currents were passed through the film, and the difference of potential between two fine wires thrust into it was measured by an electrometer, and compared with that between two other points in the same circuit separated by a known resistance[†].

Although in many respects a great improvement, this method was in one point inferior to that previously employed. The behaviour of the films was very irregular when compared with that of those previously examined by the galvanometer, although they were formed of a liquid having the same composition. Sometimes they thinned rapidly, sometimes slowly; at one time the black would appear after a comparatively short interval; at another, the film would persist for many hours without showing a trace of black. As at this time our attention had not been directed to the possible influence of the current itself in modifying the rate of thinning of the film, no special precautions were taken with regard to the current, either as to its direction or intermittence; but we now know that the apparently capricious behaviour of the films observed on many occasions was largely, if not entirely, due to want of method in managing the current.

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[*] Read December 13, 1884.

[†] "On the Electrical Resistance of Thin Liquid Films, with a Revision of Newton's Table of Colours," Phil. Trans. 1881.

We have recently made some experiments with the definite object of determining the effect upon a liquid film of passing through it a current of electricity. Some of the results obtained were communicated to Section A of the British Association at the Montreal meeting. We propose to give in this paper a somewhat more detailed account of our observations.

The liquid employed consisted either of a solution of potash soap in water, or of Plateau's *liquide glycérique*, containing a certain proportion of nitre to increase its conductivity. The films had the form of vertical cylinders, the upper and lower ring supports being of platinum, and about 33 millim. in diameter. The cylinders were generally either 30 or 40 millim. long. Occasionally other lengths were employed. Three films were under examination at the same time; two being in one glass box, the third in a separate glass box. The two that were together were supported by platinum rings identically alike and sharply bevelled at the edge; the edges of the supports of the third were much thicker and were rounded. We had thus the means of ascertaining whether any difference in the behaviour of the films was due to the form or thickness of their supports. No such difference was observed.

Each of the film-boxes was placed in the centre of a water-tank with glass sides, in order to prevent rapid changes of temperature. In all cases the films were surrounded with air saturated with the vapour of the liquid of which they were made. The constancy of the hygrometric state of the air, and that of its temperature were indicated respectively by a hair-hygrometer and a thermometer inside the glass case.

The films were blown with air which was first dried and then passed over some of the soap-solution in a wide tube. The state of the air inside the film was thus approximately the same as that on the outside.

In the earlier experiments a battery of nine Leclanché cells was used, the electromotive force of which was about 12 volts. More recently we have employed the current from a Siemens' dynamo. The current passed through a sensitive reflecting galvanometer, the deflection on the scale measuring approximately the strength of the current. This varied from about 100 microampères to half a microampère.

We began our experiments by observing the behaviour of a number of films, each 40 millim. long, formed of potash-soap solution without any glycerine, which were allowed to thin in the ordinary way, no current passing through them. In less than a minute after the adjustment of the film to the cylindrical form narrow rings of colour appeared, and white of the first order of Newton's rings was soon seen at the top, generally bordered by a narrow band of deep blue, the blue of the second order. The coloured bands did not extend beyond 10 millim. from the top, the rest of the film being colourless. This was the state of the case at the end of five or six minutes. In from eight to fifteen minutes from the moment of formation of the film a black ring appeared and slowly extended downwards. Nine films were examined, and all behaved substantially in the same way.

We now tried the effect of passing a current through the films. It is unnecessary to describe all the observations that were made, as the object of many of them was merely to obtain confirmation of previous results. A few typical cases may be described.

i. *Downward Current. Plain Potash-soap Solution.*

(1) Film 40 millim. long. A current was passed through from the moment of its formation. Broad bands of colour formed and spread with great rapidity, soon occupying the whole area of the film. After six minutes the current was 2·6 microampères (m.a.). In eleven minutes there was a ring of black, which in two minutes more increased to 3 millim. The current was then stopped.

It appears from this and a number of other experiments made in the same way that the effect of the downward current is to promote the thinning of the film. The bands are broader and spread out more rapidly than when no current is applied.

(2) A film 40 millim. long had thinned until 2·5 millim. of black were formed. Next to the black came a band of deep blue. A downward current of 5·18 m.a. was applied. The blue changed to white, the black not being altered. After nine minutes the black was still of about the same breadth and

the white had increased to 16 millim., the current being now 4·06 m.a. In two minutes after breaking the circuit the white had changed to black, the extent of which had become 19 millim., *i. e.* nearly half the length of the film.

The change from white to black in an experiment such as this is very striking: the black does not begin at the top and spread downwards as might have been expected, but the whole area of the white passes by insensible gradations into black, and it is difficult to say at times whether it is black or white. This intermediate condition between black and white can generally be obtained by accelerating the thinning of a film by a downward current until white has been formed, and then breaking the circuit and leaving the film to itself.

This and similar observations show that a downward current has the remarkable effect of rapidly thinning that part of the film which is thicker than the black; but does not necessarily affect the latter. The film is, however, put into such a condition that, on the cessation of the current, the development of the black proceeds at a rapid rate.

(3) A film 40 millim. long had a ring of black 2·5 millim. in breadth at the top. A downward current of 6·2 m.a. was applied. In one minute the black entirely disappeared, being replaced by white. The current rose to 6·5 m.a.

The conditions in this case appear to be nearly the same as in the last. In each there are 2·5 millim. black, and the strength of current applied is about the same. Nevertheless in the latter the effect is to destroy the black and increase the conductivity of the film.

This is to be explained as follows:—When a film is formed between metal supports, the thin portion of the film is not immediately in contact with the metal. There is between them a thick ring of liquid of variable length, and from this the film proper hangs. As the film thins this massive ring of liquid is maintained more or less unaltered. Experiments were made with supports of various materials, shapes, and thicknesses, with the object of determining whether these had any marked effect on the mode or rate of thinning of the films. Glass, iron, and platinum have been used, and the edges of the supports made thick and rounded or finely bevelled. Although a thick and rounded edge would support a larger quantity of liquid than a sharp edge, the thinning of the films seemed little influenced by these modifications. When therefore a downward current is passed through a film having a certain area of black immediately depending from a ring of thick liquid, the current, carrying matter with it, soon floods the black with liquid and causes it to appear first grey and then white, its thickness and therefore its conductivity increasing. In the same way may be explained the fact that when a downward current flows through a film from the moment of its formation, although the film thins more or less rapidly to the white of the first order, it generally does not show the black so soon as it would have done if no current had been flowing. So long as a thick liquid fringe remains on the upper support, liquid is being carried downwards and the film prevented from thinning beyond a certain limit. As soon as the circuit is broken this downward passage of liquid ceases, and the white of the first order rapidly thins to black. The fact that the current sometimes does and sometimes does not destroy the black may be understood by reflecting that the increase or decrease in the thickness of any part of the film depends upon whether the quantity of matter carried into it exceeds or falls short of that transported away from it in the same time. Since both these effects are produced in part by gravity and in part by the action of the current, and are also probably modified by the thickness of the different parts of the film, it is possible that very slight differences in the conditions of the experiment may determine which of the two shall obtain the predominance.

(4) Film 30 millim. long. A downward current of 24 m.a. applied from the beginning. In ten minutes the white extended more than halfway down, and the current fell to 2·5 m.a. The circuit was then broken. The white turned to black so rapidly that in less than one minute the entire transformation was effected.

In this case, the film being shorter, the same battery gave a stronger current, and the changes due to the current were accelerated.

We will now describe a few typical cases of the action of an upward current.

ii. *Upward Current. Plain Potash-soap Solution.*

(1) Film 40 millim. long. Current (9·2 m.a.) applied from the beginning. In twenty-four minutes there was a narrow band of white at the top succeeded by a narrow band of indigo-blue. Faint uniform tint below. The film was left for three quarters of an hour, but no black appeared. The current fell to 1·95 m.a. We have evidence here of the retarding action of the current, as the film would have exhibited black in ten or twelve minutes had there been no current. The current was too feeble to produce more marked changes.

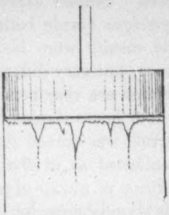
(2) Film 40 millim. long. There were 3 millim. of black and 3 millim. of white immediately below. An upward current of 4·9 m.a. was used. The lower edge of the black became blurred and indistinct, and in two minutes the black had disappeared, white taking its place. The current rose to 5·32 m.a. The circuit was then broken. Three millim. of black having been formed in seven minutes, the current was again put on (C=4·2 m.a.). The fuzziness at the edge reappeared at once, and in two minutes the black was all gone. The current rose to 4·62 m.a.

(3) Film 19 millim. long, entirely black from top to bottom. Upward current of 3·12 m.a. put on. In thirty-eight minutes the current rose to 4·23 m.a., and the film was white throughout.

(4) Film 30 millim. long. Black appeared in ten minutes. When it had increased to 5 millim. the circuit was completed. C=5·05 m.a. In one minute all the black had disappeared, and in two minutes more the film had a uniform tint throughout, while the current rose to 14·5 m.a.

(5) Film 30 millim. long. Upward current passed through from the beginning. It was not measured at first, but after five minutes its strength was 20 m.a. This increased to 28·5 m.a., which was maintained for several minutes, after which it slowly fell. The film was colourless.

The ring of liquid on the upper platinum support was seen to increase in thickness and to become wavy along its lower edge. Pendent drops were formed, pointed at the bottom,



and hanging from the liquid fringe. From the points of the drops tiny streamlets were seen flowing down the film. This is a very remarkable experiment. The up-current not only retards the thinning, but actually increases the thickness of the film. The strength of the current was not observed at first; but from the moment when it was observed until it reached its maximum it increased by over 40 per cent., and the thickness of the film must have increased in nearly the same proportion. In opposition to gravity the current carries liquid to the top of the film, where it accumulates and from which it descends in liquid veins.

The phenomena mentioned above recurred in several other films similarly treated. In some cases the film lasted long enough after the circuit was broken for black to be formed and to extend to a considerable depth; and the curious spectacle was exhibited of pendent drops of thick colourless liquid penetrating through the black to a distance varying from ½ millim. to 9½ millim.

(6) Film 30 millim. long. When the black, which appeared in ten minutes, had increased to 14 millim. a current was passed. C=1·9 m.a. In five minutes the black was reduced to 8 millim., and then the film broke. This shows that even a feeble current is, at certain stages of a film's existence, sufficient to destroy the black.

(7) The last case we may mention was one in which two films, each 30 millim. long, were formed side by side. The current from the battery was divided and passed up one and down the other film. The effect was most striking. In twelve minutes, when one of the films broke, there were 15 millim. of black in the one, while the other was thick and colourless and liquid was streaming from the top of it.

The experiments cited above were made with a solution of potash-soap (Brit. Pharm.) without any glycerine. The advantage of using such a solution is that the films formed with it grow thin with tolerable rapidity, and in the course of two or three hours several films may be observed with each apparatus. Similar experiments were carried out with *liquide glycérique* (made both with oleate of soda and potash-soap). The results were identical in kind with those enumerated above, but very different in degree. Films made with this solution are very persistent, but thin slowly. Generally three or four hours elapsed before any black appeared; and when a current was passed through, its effect was not so promptly manifested as in the case of the plain soap solution. The addition of nitrate of potassium may be partly accountable for this sluggishness, for it certainly increases the viscosity of the liquid. Nevertheless a great number of films made of the glycerine solution were observed, with currents flowing up or down. The effect of the downward current was invariably to promote, of the upward current to retard, the thinning of the film.

INDEX.

◆

A.

Page

Adjustment of resistance-coils, on the ... 47
Air, experiments on the velocity of sound in ... 228
Alterations in the electrical resistances of metallic wires, produced by coiling and uncoiling ... 235
Anemometer, an integrating ... 115
Apparatus for colour-combinations, on a new ... 200
Attached water, on salt-solutions and ... 169
Ayrton, W. E., and Perry, John, on direct-reading electro-measuring instruments, and a non-sparking key ... 59
——, ——, on the gas-engine indicator-diagram ... 149

B.

Baily, Walter, on an integrating anemometer ... 115
Bidwell, S., on some experiments illustrating an explanation of Hall's phenomenon ... 29
Blaikley, D. J., experiments on the velocity of sound in air ... 228
Boys, C. Vernon, on a magneto-electric phenomenon ... 218

C.

Campbell, Sir Archibald, and Goolden, W. T., on a "speed-indicator" for ships' propellers ... 147
Capillary multiplier, a ... 351
—— ——, method of use ... 353
Chemical affinity in terms of electromotive force, determination of 77, 275
Clark, J. W., and Lodge, O., on the phenomena exhibited by dusty air in the neighbourhood of strongly illuminated bodies ... 1
Colour-combinations, on a new apparatus for ... 200
Comparison of resistances, on a practical point in connexion with the 71
Condenser, on a method of measuring the electrical capacity of a .. 204
Copper-antimony alloys, note on the electric conductivity and other properties of the ... 53

D.

Page

Determination by electrical observations of the period of a tuning-fork 204
—— of chemical affinity in terms of electromotive force 77, 275
Direct-reading electro-measuring instruments, and a non-sparking key 59
Drops, note on a point in the theory of pendent 355
Dusty air in the neighbourhood of strongly illuminated bodies, phenomena exhibited by 1

E.

Electric conductivity and other properties of the copper-antimony alloys, note on the 53
—— current in modifying the rate of thinning of a liquid film, the influence of an 357
Electrical capacity of a condenser, on a method of measuring the .. 204
—— resistances of metallic wires, on the alterations in the, produced by coiling and uncoiling 235
Electro-measuring instruments, direct-reading, and a non-sparking key 59
Electromotive force, determination of chemical affinity in terms of 77, 275
Eutexia, on 124
Experiments illustrating an explanation of Hall's phenomenon 29
—— on the velocity of sound in air 228

F.

Film, the influence of an electric current in modifying the rate of thinning of a liquid 357

G.

Gas-engine indicator-diagram, on the 149
Glazebrook, R. T., on a method of measuring the electrical capacity of a condenser, and on the determination by electrical observations of the period of a tuning-fork 204
Goolden, W. G., and Campbell, Sir Archibald, on a "speed-indicator" for ships' propellers 147
Guthrie, F., on Eutexia 124
——, on salt-solutions and attached water 169
——, on some thermal and volume changes attending mixture 249

H.

Hall's phenomenon, note on 74
—— ——, some experiments illustrating an explanation of 29
Hoffert, H. H., on a new apparatus for colour-combinations 200

Page
Hopps, James, on the alterations in the electrical resistances of metallic wires, produced by coiling and uncoiling 235
Howard, A., and Illingworth, B., on the thermal relationship between water and certain salts 212

I.

Illingworth, B., and Howard, A., on the thermal relationship between water and certain salts 212
Illuminated bodies, on the phenomena exhibited by dusty air in the neighbourhood of strongly 1
Indicator-diagram, the gas-engine 149
Influence of an electric current in modifying the rate of thinning of a liquid film, on the 357
Integrating anêmometer, on an 115

K.

Kamensky, G., note on the electric conductivity and other properties of the copper-antimony alloys 53

L.

Liquid film, the influence of an electric current in modifying the rate of thinning of a 357
Lodge, O., and Clark, J. W., on the phenomena exhibited by dusty air in the neighbourhood of strongly illuminated bodies 1

M.

M'Leod, Herbert, preliminary notice of a new sunshine-recorder.... 216
Magneto-electric phenomenon, on a 218
Metallic wires, on the alterations in the electrical resistances of, produced by coiling and uncoiling 235
Method of measuring the electrical capacity of a condenser, and on the determination by electrical observations of the period of a tuning-fork 204
Modified resistance-balance, on a 121
Modifying the rate of thinning of a liquid film, the influence of an electric current in 357
Multiplier, a capillary 351

N.

Non-sparking key, direct-reading electro-measuring instruments, and a 59
Note on a point in the theory of pendent drops 355
—— on Hall's phenomenon 74
—— on the electric conductivity and other properties of the copper-antimony alloys 53

O. Page

Observations of the period of a tuning-fork, on the determination by electrical ... 204

P.

Pendent drops, note on a point in the theory of ... 355
Perry, John, and Ayrton, W. E., on direct-reading electro-measuring instruments, and a non-sparking key ... 59
——, ——, on the gas-engine indicator-diagram ... 149
Phenomena exhibited by dusty air in the neighbourhood of strongly illuminated bodies ... 1
Point in the theory of pendent drops, note on a ... 355
Practical point in connexion with the comparison of resistances, on a 71
Preliminary notice of a new sunshine-recorder ... 216

R.

Rate of thinning of a liquid film, the influence of an electric current in modifying the ... 357
Reinold, A. W., and Rücker, A. W., on the influence of an electric current in modifying the rate of thinning of a liquid film ... 357
Resistance-balance, on a modified ... 121
—— coils, on the adjustment of ... 47
Resistances, on a practical point in connexion with the comparison of 71
Rücker, A. W., and Reinold, A. W., on the influence of an electric current in modifying the rate of thinning of a liquid film ... 357

S.

Salt-solutions and attached water ... 169
Shaw, W. N., on a practical point in connexion with the comparison of resistances ... 71
Sound in air, experiments on the velocity of ... 228
"Speed indicator" for ships' propellers, on a ... 147
Sunshine-recorder, preliminary notice of a new ... 216

T.

Theory of pendent drops, note on a point in the ... 355
Thermal and volume changes attending mixture, on some ... 249
—— relationship between water and certain salts ... 212
Thinning of a liquid film, the influence of an electric current in modifying the rate of ... 357
Thompson, C., and Wright, C. R. Alder, on the determination of chemical affinity in terms of electromotive force ... 77, 275
Thompson, Silvanus P., on a modified resistance-balance ... 121
——, on the adjustment of resistance-coils ... 47
Tomlinson, H., note on Hall's phenomenon ... 74
Tuning-fork, on the determination by electrical observations of the period of a ... 204

V.

Page

Velocity of sound in air, experiments on the 228
Volume changes attending mixture, on some thermal and 249

W.

Water and certain salts, on the thermal relationship between 212
Worthington, A. M., note on a point in the theory of pendent drops 355
——, on a capillary multiplier 351
Wright, C. R. Alder, and Thompson, C., on the determination of chemical affinity in terms of electromotive force 77, 275

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PROCEEDINGS

AT THE

MEETINGS OF THE PHYSICAL SOCIETY

OF LONDON.

SESSION 1884-85.

February 9th, 1884.

Dr. F. Guthrie, President, in the Chair.

The following communication was made :—

"On the Phenomena presented by Bodies when highly illuminated in Dusty Air." By Dr. O. J. Lodge and Mr. J. W. Clark.

February 23rd, 1884.

Dr. F. Guthrie, President, in the Chair.

The following were elected Members of the Society :—

E. F. J. Love; James Grundy; Rev. F. J. Smith, B.A.; F. R. Barrell, B.A.

The following communications were made:—

"On the Adjustment of Resistance-Coils;" and "On a Modified Resistance-Balance." By Prof. S. P. Thompson.

"On the Difference of Potentials required to give Sparks in Air." By Prof. G. Carey Foster and Mr. A. H. Fison.

"On some Experiments with a Magnetized Watch." By Prof. G. Forbes.

March 8th, 1884.

Dr. F. Guthrie, President, in the Chair.

The following communications were made:—

"On the Electrochemical Equivalent of Silver, and the Absolute E.M.F. of a Clark's Cell." By Lord Rayleigh.

"Experiments illustrating an Explanation of Hall's Phenomenon." By Mr. Shelford Bidwell.

March 22nd, 1884.

Dr. F. Guthrie, President, in the Chair.

The following communications were made:—

"On an Explanation of Hall's Phenomenon." By Prof. S. P. Thompson and Mr. C. C. Starling.

"Note on Hall's Phenomenon." By Mr. Herbert Tomlinson.

"On Hall's Effect in Tin." By Mr. Shelford Bidwell.

"On some Properties in Electromagnetics." By Prof. S. P. Thompson and Mr. W. M. Moorsom.

April 26th, 1884.

Dr. F. Guthrie, President, in the Chair.

The following were elected Members of the Society:—

Richard Inwards, F.R.A.S.; Arthur Prince Chattock.

The following communications were made:—

"On the Indicator-Diagram of a Gas-Engine." By Profs. Ayrton and Perry.

"On a Metrical Barometer." By Dr. W. H. Stone.

May 10th, 1884.

The Meeting was held in the Mason College, Birmingham.

Dr. F. GUTHRIE, President, in the Chair.

The following were elected Members of the Society:—

W. STEPNEY RAWSON, M.A.; Lieut. E. J. W. SLADE, R.N.

The following communications were made:—

"On an Illustration of the Refraction of Waves." By Prof. J. H. POYNTING.

"On an Oxyhydrogen Lantern suitable for Lecture-experiments." By Mr. C. J. WOODWARD.

"On the Effect of Temperature on the Mixing of Liquids." By Dr. F. GUTHRIE.

May 24th, 1884.

Prof. W. G. ADAMS, Vice-President, in the Chair.

The following was elected a Member of the Society:—

F. C. PHILLIPS.

The following communications were made:—

"On Eutexia." By Dr. F. GUTHRIE.

"On an Immersion-Galvanometer;" and "On Kohlrausch's Metre-Bridge for Alternating Currents." By Dr. W. H. STONE.

"On a Speed Indicator." By Mr. W. T. GOOLDEN.

"On a Speed Indicator." By Mr. WALTER BAILY.

June 14th, 1884.

Dr. F. GUTHRIE, President, in the Chair.

The following was elected a Member of the Society:—

ARTHUR STANLEY BUTLER.

The following communications were made:—

"On a new Apparatus for Colour-Sensations." By Mr. H. H. HOFFERT.

"Experiments on the Velocity of Sound in Tubes." By Mr. D. J. Blaikley.

"On the Thermal Relationship of Water and certain Salts." By Messrs. B. Illingworth and A. Howard.

June 28th, 1884.

Dr. F. Guthrie, President, in the Chair.

The following was elected a Member of the Society:—

W. S. Hemsley.

The following communications were made:—

"On the Practical Use of the Silver Voltameter for the Measurements of Electric Currents." By Lord Rayleigh.

"On a Colour-mixing Apparatus founded on Double Refraction." By Lord Rayleigh.

"On a Phenomenon in Electromagnetic Induction." By Mr. C. V. Boys.

"On the Alterations in the Electrical Resistances of Metallic Wires, produced by Coiling and Uncoiling." By Mr. J. Hopps.

"On the Absolute Determination of the Electrical Capacity of a Condenser, and on a Method of finding the Period of Vibration of a Tuning-fork." By Mr. R. T. Glazebrook.

"On a Sunshine-Recorder." By Prof. McLeod.

November 8th, 1884.

Prof. W. E. Ayrton, Vice-President, in the Chair.

The following was elected a Member of the Society:—

Kavargee Dadabhoy Nargamvala.

The following communications were made:—

"On certain Phenomena attending Mixture." By Dr. F. Guthrie.

"On certain Voltaic and Thermo-voltaic Constants." By Dr. C. R. Alder Wright and Mr. C. Thompson.

November 22nd, 1884.

Dr. F. Guthrie, President, in the Chair.

The following was elected a Member of the Society:—

James Beasher.

The following communications were made:—

"On the Permanence of some Electrical Standards;" "On some Experiments on the Effects of Moisture in modifying the Refraction of Plane-Polarized Light by Glass;" and "On a Spectro-Photometer." By Mr. R. T. Glazebrook.

"Note on a Point in the Theory of Pendent Drops;" and "On a Capillary Multiplier." By Mr. A. M. Worthington.

"On a new Solar Eyepiece." By Mr. A. Hilger.

December 13th, 1884.

Dr. F. Guthrie, President, in the Chair.

The following communications were made:—

"On the Influence of an Electric Current on the Rate of Thinning of a Liquid Film." By Profs. A. W. Reinold and A. W. Rücker.

"On a Tuning-fork Interrupter and Commutator." By Dr. W. H. Stone.

"On a new Oxyhydrogen Lantern-Microscope." By Mr. Lewis Wright.

January 24th, 1885.

Dr. F. Guthrie, President, in the Chair.

The following were elected Members of the Society:—

A. Howard; J. C. McConnel, B.A.;
A. M. Worthington, M.A.; J. Rose-Innes, B.Sc.

The following communications were made:—

"Lecture-Experiments on Spectrum Analysis." By Mr. E. Cleminshaw.

"On an Instrument illustrating the Equilibrium of three Forces." By Mr. Walter Baily.

"On the Poiograph." By Mr. C. H. Hinton.

Annual General Meeting.

February 14th, 1885.

Prof. F. GUTHRIE, President, in the Chair.

The following Report of the Council was read by the President :—

In presenting their Annual Report the Council congratulate the Society on the valuable work which has been brought before the Meetings during the past year in the 43 separate Communications which have been made. New subjects for investigation have been brought forward by our President's papers on Alloys and Mixtures, and by Professors Reinold and Rücker's communication on the Effect of an Electric Current on a Soap Film, and by Mr. Glazebrook's paper on the Optical Effect of Moisture on the Surface of Glass; while discussions of unsettled questions of importance have been introduced, among which may be mentioned that on Dusty Air by Dr. Lodge, and those on Hall's Phenomenon by Mr. Bidwell, Professor S. P. Thompson, and Mr. H. Tomlinson. It will, however, be a matter of regret to Members of the Society that some of these communications had been previously made elsewhere, and consequently Members will not be able to receive a Report of them in our 'Proceedings.' The Council trust that it may become more and more the custom for our Members to communicate their Physical work in the first instance to this Society, so that our 'Proceedings' may become a fairly complete record of the original work done in England in the Department of Physics.

The Society held a Meeting last summer in Birmingham, which gave those Members who attended an opportunity of visiting some of the most interesting Manufactories and Institutions of that town; and the Council desire to express their thanks to the Members residing there for the efficiency of the arrangements which were made.

The following circular, which has been issued to Members of the Society, explains the action which the Council have taken with respect to the International Inventions Exhibition :—

"Physical Laboratory,
"South Kensington,
"January 9, 1885.

"DEAR SIR,—The Members of this Society are doubtless aware that in the International Exhibition of Inventions to be held at South Kensington in the course of this year, a prominent position

will be assigned to Collections of Scientific Apparatus. It has appeared to the Council of this Society very desirable that the Society should avail itself of the opportunity thus afforded of exhibiting in a collected form any apparatus, diagrams, and appliances which relate to communications made to the Society, so as to put in evidence the work done by the Society since its foundation. The Council have accordingly applied for space for such an exhibition, to be held under their direction; and members are requested to send to one of the Secretaries of this Society the particulars of whatever they desire to exhibit. As the space at the disposal of the Society is necessarily limited, such particulars should be sent as early as possible, together with an approximate estimate of the space required. The exhibition, if made worthy of the Society, must involve some expense in arrangement and supervision, the disbursement of which out of the ordinary funds of the Society might entail postponement of the publication of the books which the Society has undertaken to issue; and, to avoid any such postponement, the Council invite from members subscriptions, which would of course be purely voluntary, for the purpose of defraying the additional expenditure.

"Yours faithfully,
A. W. Reinold, } *Hon. Secs.*"
Walter Baily, }

The Council are confident that Members will cordially assist them in their endeavours to make this Exhibition of the work of the Society as complete and satisfactory as possible. The space allotted to the Society is 36 feet long by 3 feet deep.

The Library consists of 660 bound volumes; 154 unbound and 300 separate pamphlets. During the past Session 100 volumes have been bound, and about 30 are ready for binding. The Library has been enriched since the last Report by many valuable gifts, amongst which may be mentioned:—'The Memoirs of Coulomb,' presented by the Physical Society of France; 'Ronald's Catalogue,' presented by the Society of Telegraph Engineers; 'The Observatory,' by the Editor; Proceedings of the Cambridge Philosophical Society, by the Society; 'Proceedings' and 'Transactions' of the Royal Society of London, by one of our Members; Proceedings of the Royal Society of Edinburgh, also by a Member.

Early in the current year the first volume of Joule's complete works was issued to the Members; and the Society may justly congratulate itself as having been the means of bringing out a work of such historical importance. The second volume will contain the researches of Dr. Joule in conjunction with other scientific men. The first instalment of the copy has been received from Dr. Joule, and is now in the hands of the printer; and it is hoped that the volume will be issued during the present year.

A portion of the translation of Volta has been put in type; this must for the present be in abeyance until the Society meet with a person competent to undertake the editing of that already done and the translation of the rest.

It may here be observed that all the funds which the Society can dispose of for its reprints will be absorbed in the production of the second volume of Joule. Considering how large a number of Physicists have received the first volume as Members of the Society, the sale to the Public is not unsatisfactory; and it is confidently hoped that this sale will continue, and even increase when the work is complete. The Council would urge upon Members the importance of furthering this sale in any way they can, as on the returns thus obtained must depend the extent to which the Society can venture in this direction.

The Council regret to announce the deaths of five Members—Mr. H. R. Droop, Mr. W. R. Browne, Mr. J. F. Iselin, and Mr. R. Angus Smith.

Henry Richmond Droop, who, on his father's side, was of a North German family, was at school at Marlborough College. Thence he proceeded to Trinity, Cambridge. He took his Bachelor's degree in 1854 as third Wrangler, Mr. Routh and the late Professor Maxwell being senior and second. In due course he was elected Fellow of Trinity, and appointed a mathematical lecturer. He voluntarily resigned his Fellowship from an honourable scruple at its retention when his private means enabled him to dispense with the emolument as a means of support. His lectureship he gave up that he might study law. He became an accomplished and scientific conveyancer, and attained as much practice as he cared for. But his favourite studies were the antiquities of Ecclesiastical Post-Reformation Law, and the theory of Proportional Representation. On the former he was much consulted, both professionally and also as a friend, by barristers engaged on the anti-ritualistic side. He had made himself a thorough master of all the intricate learning of the subject. He took even a deeper interest in the defence of the parliamentary rights of minorities. On this and on ecclesiastical topics he published several thoughtful and subtle papers. He became a Member of this Society in 1879; and in the course of the long and distressing illness from which he died, he communicated to the

Society the interesting paper on Colour Blindness, which is published in the fifth volume of our 'Proceedings.' He died on the 21st of March 1884, at the age of 51.

WALTER RALEIGH BROWNE, born in 1842, was the third son of the late Rev. T. Murray Browne, Vicar of Almondsbury, and Honorary Canon of Gloucester Cathedral. He entered at Trinity College, Cambridge, in 1861, and obtained a foundation Scholarship in 1863. He took his degree in 1865, being 19th Wrangler and bracketed 10th Classic. While at Cambridge he obtained the Wrangham and Leigh Gold Medal and Prize, and in two successive years the Dealtry and College Prizes for Greek Testament.

Mr. Browne was elected an Associate of the Institution of Civil Engineers in 1868, and became a Member in 1879. For a paper on "The Strength of Lock Gates," read before the Institution in 1871, a Telford Premium was awarded to him, and in 1876 his paper "On Railway Rolling-Stock," being placed first in order of merit among those read during the Session, gained a Telford Medal and Premium.

Having completed his apprenticeship as an Engineer, he became in 1874 Managing Director of the Bridgewater Engineering Company; and when, two years later, depression in trade caused these works to be closed, he was appointed Secretary to the Institution of Mechanical Engineers. This appointment he held for six years, and to the energy and ability with which he discharged his duties the Institution was largely indebted for the progress which it made during that period. He resigned the Secretaryship in 1884, and entered upon the profession of a Consulting Engineer under very favourable circumstances and with every prospect of success. In August last he went with his wife to Canada to attend the meeting of the British Association. Shortly after his arrival at Montreal he was seized with typhoid fever, and inflammation of the lungs supervening after a few days, his case became hopeless, and he died on September 4, at the early age of 42 years.

In addition to the professional interest which Mr. Browne took in matters relating to Engineering, as evidenced by his important communications to the Institutions of Civil and Mechanical Engineers, the Iron and Steel Institute, and the technical journals, he devoted considerable attention to other branches of science. He joined the Physical Society in 1880; and his papers on "Action at a Distance," "Central Forces and the Conservation of Energy," "The Reality of Force," and "The Movements of Glaciers," with the interesting discussions by which they were followed, will be fresh in the memories of many of our Members. He was a Fellow or Member of the Geological, Royal Geographical, Philological, Psychical Research, Aristotelian, and the Christian Evidence Societies. In all these he took an active interest, and to all, as also to the Royal Society, the Society of Arts, and the Church Congress, he contributed valuable papers. Many articles, signed and unsigned, which have appeared in the 'Engineer,' 'Nature,' 'Philosophical Magazine,' 'Electrician,' 'Athenæum,' 'Builder,' and 'Church Quarterly Review,' are from the pen of Mr. Browne. He was the author of two text-books on Mechanics; and he published admirable translations of Clausius' 'Mechanical Theory of Heat,' and Schwachhofer's 'Fuel and Water.'

Mr. Browne was well known as a philanthropist, especially for the interest which he took in the promotion of emigration. He was also an active member of the Central Committee of the Discharged Prisoners' Aid Society.

To those who were personally acquainted with him Mr. Browne was known as a man of kindly and genial disposition, with a wide knowledge extending over a great variety of subjects, and as one whose advice and assistance were always at the service of those requiring them, no matter at what inconvenience to himself. The bare record here given shows how full of work and usefulness was the life which has been cut short.

Robert Henry Sabine was born at Dorchester in 1837. He was originally intended for the legal profession; and was for some time employed in the office of his father, who was a solicitor. But having a distaste for law and a marked inclination for scientific pursuits, he obtained an introduction to the late Sir William Siemens, who in 1858 engaged him as an assistant electrician. After two or three years, in the course of which he took part in some important experimental work, Mr. Sabine was transferred to the establishment of Messrs. Siemens and Halske at Berlin, where he was engaged principally on work in connection with submarine cables. He remained in the employment of this firm until 1867, when he started on his own account as a consulting electrical engineer. Shortly afterwards he undertook the management of some works belonging to Sir Charles Wheatstone. These subsequently developed into the British Telegraph Company, of which Mr. Sabine was for some years Managing Director. He afterwards resumed the business of an electrical engineer, which he continued to carry on until his death.

Mr. Sabine was the author and joint-author of several important books on electrical subjects. Perhaps the most valuable and best known of these is the collection of 'Electrical Tables and Formulæ,' which he published in conjunction with Mr. Latimer Clark. His work was mostly of a practical nature; but the 'Proceedings' of the Royal Society and the 'Philosophical Magazine' contain papers by him upon purely physical subjects, those relating to the behaviour of selenium under the action of light being especially interesting.

As son-in-law of the late Sir Charles Wheatstone, Mr. Sabine was able to give the Council of the Physical Society material assistance in the preparation of Wheatstone's Scientific Papers for republication. He was one of the original Members of this Society.

He died on October 24, 1885, at the age of 47, after several months' severe illness.

J. F. ISELIN was born in Cadogan Place, London, on August 20, 1832. Two years of his boyhood were passed in Switzerland. At the age of thirteen he became a pupil in the Grammar School, Plymouth. Thence he went to Corpus Christi College, Cambridge, where he graduated in Honours in 1855, being 17th Wrangler. After four years' service as Mathematical Master in Stockwell Grammar School, he received the appointment of Inspector of Schools under the Science and Art Department; and he acted also as Assistant Examiner in Pure Mathematics in the years 1870, 1872, and 1873. It is understood that his reports showed extreme care and conscientiousness, and a great grasp of the questions which presented themselves to him. His valuable services were enlisted in the organization in London and the provinces of exhibitions of an educational character. He became a Member of this Society in 1878.

In March 1880 he was appointed Assistant Director for Science. He died, after some months' illness, on the night of November 1, 1884.

While the absorbing nature of Mr. Iselin's official duties prevented him from contributing to the common store of scientific knowledge, the very performance of those duties, as he understood them to be, has had indirectly a most beneficent effect upon Science Teaching. Of a retiring and modest disposition, the circle of his friendship was small. The few within that circle have lost by his death a single-hearted friend. The cause of Education has lost an able and most loyal and valuable servant.

Robert Angus Smith was born near Glasgow in 1817. After passing through the High School and University of that city, he went to Giessen, and studied chemistry under Liebig. In 1842 he settled at Manchester as Consulting Chemist, and became the author of many papers on the air and water of towns. In 1863 he was appointed Inspector-General of the Alkali Works; and on the passing of the Rivers Pollutions Act he was made Inspector for England, and afterwards for Scotland. He became a Fellow of the Royal Society in 1857, and received the degree of LL.D. of Edinburgh in 1882. He was one of the original Members of this Society.

The Treasurer made the Financial Statement given below.

The Society then proceeded to the election of Officers and other Members of Council for the ensuing year. The Council was constituted as follows:—

President.—Prof. F. Guthrie, Ph.D., F.R.S.

Permanent Vice-Presidents.—Dr. J. H. Gladstone, F.R.S.; Prof. G. C. Foster, F.R.S.; Prof. W. G. Adams, M.A., F.R.S.; Sir William Thomson, D.C.L., LL.D., F.R.S.; Prof. R. B. Clifton, M.A., F.R.S.

Other Vice-Presidents.—Prof. W. E. Ayrton, F.R.S.; Shelford Bidwell, M.A., LL.B.; Lord Rayleigh, M.A., F.R.S.; Prof. W. Chandler Roberts, F.R.S.

Secretaries.—Prof. A. W. Reinold, M.A., F.R.S.; Walter Baily, M.A.

Treasurer.—Dr. E. Atkinson.

Demonstrator.—Prof. F. Guthrie, Ph.D., F.R.S.

Other Members of Council.—C. Vernon Boys; Conrad W. Cooke;

Prof. G. Forbes, M.A., F.R.S.E.; Prof. F. Fuller, M.A.; R. T. Glazebrook, M.A., F.R.S.; J. Hopkinson, M.A., D.Sc., F.R.S.; Prof. H. McLeod, F.R.S.; Prof. J. Perry, M.E.; Prof. J. H. Poynting, M.A.; Prof. S. P. Thompson, D.Sc.

Votes of thanks were passed to the Lords of the Committee of Council on Education; to the President and other Officers of the Society; and to the Auditors.

THE TREASURER IN ACCOUNT WITH THE PHYSICAL SOCIETY, FROM JANUARY 1ST, 1883, TO DECEMBER 31ST, 1884.

Dr.	£	*s.*	*d.*	£	*s.*	*d.*
Balance in Bank, January 1, 1884				62	8	0
„ due by Treasurer, Jan. 1, 1884				5	6	0
13 Entrance-Fees	13	0	0			
1 Subscription for 1880	1	0	0			
2 Subscriptions for 1881	2	0	0			
6 „ 1882	6	0	0			
16 „ 1883	16	0	0			
116 „ 1884	116	0	0			
Life Composition	50	0	0			
				204	0	0
One year's Dividend on £400 Furness 4 per cent. Debenture Stock, less Income Tax	15	13	4			
One year's Dividend on £460 Midland 5 per cent. Preference Stock, less Income Tax	22	10	4			
One year's Dividend on £200 Metropolitan Board of Works Stock, less Income Tax	6	17	4			
One year's Dividend on £200 Lancaster Corporation Stock	7	16	8			
				52	17	8
				324	11	8
Sale Account:—						
Joule (vol. i.)	79	2	0			
Wheatstone	7	10	6			
Proceedings	8	0	0			
	94	12	6			
Commission	9	9	6			
				85	3	0
				409	14	8

Cr.	£	*s.*	*d.*	£	*s.*	*d.*
Taylor and Francis:—						
Proceedings, vol. v. (part 5), vol. vi. (parts 1 & 2)	101	15	6			
Postage and addressing	9	18	3			
Members' separate copies	20	19	0			
Miscellaneous printing	21	10	4			
				154	3	1
Reprint Account	50	0	0			
Balance of Account	73	19	0			
				123	19	0
Reports of Meetings				14	13	6
Williams and Norgate	9	6	0			
Taylor and Francis	3	14	0			
'Electrical Review'	0	5	0			
				13	5	0
Representatives of Mr. Franklin on account of translation of Volta				15	0	0
Chapman:—Attendance at Meetings				8	1	3
Petty Cash:—						
Mr. Reinold	2	10	2			
Mr. Baily	0	18	6			
Mr. Atkinson	1	13	4			
				5	2	0
Meeting at Birmingham				0	15	2
Cheque Book				0	2	6
Balance in Bank				73	11	7
„ due by Treasurer				1	1	7
				£409	14	8

Audited and found correct,

E. R FESTING,
C. RICHARDSON, } *Auditors.*

London, February 1st, 1885.

PROPERTY ACCOUNT OF THE PHYSICAL SOCIETY.

Assets.	£	s.	d.	Liabilities.	£	s.	d.
Balance in Bank	73	11	7	Balance	1511	13	2
„ due by Treasurer	1	1	7				
Estimated Subscriptions due	36	0	0				
£400 Furness 4 per cent. Debenture Stock	412	0	0				
£460 Midland 5 per cent. Preference Stock	565	0	0				
£200 Metropolitan Board of Works Stock	210	0	0				
£214 Lancaster Corporation Stock	214	0	0				
	£1511	13	2		£1511	13	2

We have examined the above Account, and also the Securities at the Bank, and find the same to be correct.

London, February 1st, 1885.

E. R. FESTING,
C. RICHARDSON, } *Auditors.*